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LXXIII.—ON THE PRODUCTS OBTAINED BY THE ACTION OF NITRIC ACID UPON BROMTRINITROPHENYLMALONIC ESTER.

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Our attention was first called to this subject by the appearance of a vivid red color when common strong nitric acid was used to set free bromtrinitrophenylmalonic ester from its sodium salt, whereas no such color was observed if hydrochloric or sulphuric acid was used in place of nitric. Upon studying this action, we soon found that a new compound was formed, which could also be obtained from the free bromtrinitrophenylmalonic ester by treating it with hot nitric acid for a few minutes,[1] or for some hours in the cold; the free ester therefore acts with nitric acid less readily than its salt, for with that the color appeared immediately. The further study of this compound (which was obtained in colorless prisms) proved that its formula was $C_6HBr(NO_2)_2.C.NO_2.(CO.OC_2H_5)_2$; that is, that it had been formed from the bromtrinitrophenylmalonic ester by replacing one of its atoms of hydrogen by the group NO_2. We have also obtained the following similar derivatives: from the bromdinitrophenylmalonic ester

[1] A preliminary account of this substance forms part of a paper by G. D. Moore and one of us (This Journal 12, 7). The statements made there are superseded by this paper.

$C_6H_2Br(NO_2)_2.C.NO_2.(CO.OC_2H_5)_2$, melting-point 111°, and from the trinitrophenylenedimalonic ester,

$$(NO_2)_2 > C_6 < \begin{matrix} C(NO_2)(CO.OC_2H_5)_2 \\ H \quad\quad CH(CO.OC_2H_5)_2 \end{matrix},$$

also melting at 111°, so that the reaction seems to be a general one. The position of the group NO_2 introduced by the action of nitric acid was determined by the study of the acidity of these compounds. In the bromtrinitrophenylmalonic ester $C_6HBr(NO_2)_2.CH(CO.OC_2H_5)_2$ there are only two atoms of hydrogen, one on the benzol ring, the other on the side-chain; if the first of these were replaced by the nitro group, the effect, if any, would be to increase the acidity of the compound; whereas, if the atom of hydrogen on the side-chain were replaced, the substance would cease to show acid properties, as the nitro group would have taken the place of the only atom of hydrogen which can be replaced by a metal. Upon studying the behavior of the new compound with alkaline reagents, we found that none of them affected it in aqueous solution, and that it was acted on only by sodic hydrate or ethylate in alcoholic solution, thus showing a marked contrast to the behavior of bromtrinitrophenylmalonic ester, which is acid enough to decompose sodic carbonate in aqueous solution. As just stated, sodic hydrate or ethylate does act upon our substance, but the red solution formed by the sodic ethylate was proved to contain sodic nitrite, and therefore the formation of the red salt was preceded by the removal of the group NO_2, which proves that this radicle has replaced the hydrogen of the side-chain, as represented in the formula given above. This result was confirmed by the study of the compound $C_6H_2Br(NO_2)_2.C.NO_2.(CO.OC_2H_5)_2$, which proved even less susceptible to the action of alkalies than the corresponding trinitro-compound. The replacement of the hydrogen in the malonic ester radicle is not at all strange, since Franchimont and Klobbie[1] have found that nitric acid converts malonic ester into nitromalonic ester.

To determine whether our substances were nitro-compounds, that is, with the radicle NO_2 attached to the side-chain by its nitrogen, or nitrites, that is, with the radicle attached by one of its atoms of oxygen, we considered in the first place the further

[1] Ber. d. chem. Ges. **23**, Ref. 62 from Recueil trav. chim. **8**, 283. For a discussion of the effect of different radicles upon the action of nitric acid on fat substances, see Franchimont: Ber. d. chem. Ges. **20**, Ref. 689 from Recueil trav. chim. **6**, 224, and Ber. d. chem. Ges. **23**, Ref. 64 from Recueil trav. chim. **8**, 307.

action of nitric acid upon the compound $C_6HBr(NO_2)_2.C.NO_2.(CO.OC_2H_5)_2$, which converted it after warming for three hours into $C_6HBr(NO_2)_2.C.OH.(CO.OC_2H_5)_2$, that is, the bromtrinitrotartronic ester; the reaction seemed to run smoothly, and the yield was 40 per cent. of the theoretical. A similar change was produced by heat; when exposed to a temperature of 124°–126° the substance melted, turned blood-red, and gave off a great deal of gas, with a striking increase in volume at the same time.[1] A study of the gases showed that a part of the substance had undergone complete decomposition, as they contained bromine; the residue, however, furnished a considerable amount of the substituted tartronic ester mentioned above. The action therefore has a certain resemblance to the conversion of the nitrate of tartaric acid into tartronic acid. These easy conversions of the compound containing the group NO_2 into the corresponding tartronic ester can be best explained on the theory that this group is attached to the side-chain by oxygen, but cannot be considered as a strict proof of this point. Accordingly we have reduced with tin and hydrochloric acid the substance $C_6H_2Br(NO_2)_2.C.NO_2.(CO.OC_2H_5)_2$ (selected because it can be obtained more easily than the trinitro-compound), and have found that it yields ammonic chloride and a substance having the formula $C_6H_2.NH_2.(CH.OH.CO.NH)HCl$, that is, the chloride of amidoxyoxindol; there can be no doubt, therefore, that the group NO_2 is attached to the side-chain by one of its atoms of oxygen, and the substances are nitrites and not nitromalonic esters.

One of the most striking properties of the nitrite of bromtrinitrophenylmalonic ester is its slight stability. As has been already stated, it decomposes rapidly, with change of color and evolution of gas, at 124°–126°, but it is not necessary to heat to this temperature to bring about the decomposition, as it also takes place slowly at 100°, and partially even at 70°. Boiling with alcohol decomposes the substance completely, and boiling water produces a similar but less complete change. The nitrites of the corresponding dinitro-compound and of the trinitrophenylenedimalonic ester are much more stable.

As has been stated above, the nitrite of bromtrinitrophenylmalonic

[1] These phenomena shown by our substance in melting, as well as many of its other properties, are very similar to those observed by Gabriel in the cases of the benzylidenephthalide dinitrite, Ber. d. chem. Ges. **18**, 1255, and the ethindiphthalide dinitrite, Ber. d. chem. Ges. **19**, 837, which confirms the view that our substance is a nitrite.

ester, if warmed for three hours with strong nitric acid, or heated alone to its decomposition-point, yields a product in which the radicle of the nitrous acid has been replaced by hydroxyl, and which is therefore bromtrinitrophenyltartronic ester; this substance melts at 156°, and possesses marked acid properties. It is not necessary, however, to make it from the nitrite, as the bromtrinitrophenylmalonic ester is converted directly into it by warming for three hours with nitric acid. This therefore is a case of the direct oxidation of tertiary hydrogen to hydroxyl,[1] and, as we have succeeded in isolating the intermediate product, our work throws some light on the mechanism of the reaction, showing that it consists in the case of nitric acid of the formation of a nitrite, followed by its saponification to the hydroxyl compound.

$C_6H(C_6H_5NH).(NO_2)_2.C.NO_2.(CO.OC_2H_5)_2$, the nitrite of anilidotrinitrophenylmalonic ester, was obtained by the action of aniline on the corresponding bromine compound; it forms red rhombohedra, which melt at 119°, decomposing at one degree higher, and shows marked acid properties, which must be due to the effect of the three nitro-groups upon the hydrogen attached to the nitrogen in the anilido-group, since, as has already been stated, the corresponding bromine compound forms no salts. This conclusion was confirmed by the study of the anilidotrinitrotoluol, which contains no other hydrogen capable of being replaced by a basic radicle, and yet formed the sodium salt $C_6.CH_3.H(C_6H_5.NNa).(NO_2)_2$. As was to be expected, however, this toluol compound was not so acid as the nitrite of anilidotrinitrophenylmalonic ester, which contains such a very negative radicle in place of the methyl.

The anilidotrinitrotartronic ester was also made from the corresponding bromine compound, and was obtained in two modifications: one, formed at higher temperatures, appeared in orange-red prisms melting at 143°, the other in rounded masses of yellow needles melting at about 122°. Both show the same percentage composition on analysis, and one is easily converted into the other; the yellow into the red by allowing the alcoholic solution to crystallise at about 60°, by heating the solid a little below its melting-point, or by boiling it with water; the red into the yellow by solution in glacial acetic acid and precipitation with water. Unfortunately we have not succeeded in determining the molecular

[1] Richard Meyer: Ann. Chem. (Liebig) **219**, 234; **220**, 1; J. Bredt: Ber. d. chem. Ges. **14**, 1780.

weights of these substances, as we have not yet found a solvent that gives satisfactory results with Raoult's method. The work on these substances will be continued in this laboratory, especially with a view to determining whether the nitrogen is the cause of the isomerism (if they are not polymers), but we may say now that this does not seem very probable to us on account of the striking resemblance in properties[1] between our two substances and the two forms of benzilorthocarbonic acid described by Graebe.[2]

The anilidotrinitrophenyltartronic ester forms salts with one atom, $C_6H(C_6H_5.NH).(NO_2)_3C.OM.(CO.OC_2H_5)_2$, or with two atoms of univalent basic radicles, $C_6H(C_6H_5.NM)(NO_2)_3C.OM.(CO.OC_2H_5)_2$. To our great surprise, the disodic salt was formed even when the ester was present in large excess. This tartronic ester is much more strongly acid than the anilidotrinitrophenylmalonic ester (melting-point 133°), a fact which confirms the formula assigned to it. We may add that we have failed in all our attempts to convert anilidotrinitrophenylmalonic ester into its nitrite, or the corresponding tartronic ester, by the action of nitric acid.

We have also tried without success to convert the bromdinitrophenylmalonic ester into dinitrophenylenedimalonic ester by the further action of sodium-malonic ester.

The remainder of the paper contains the experimental details of the work.

Preparation of Tribromtrinitrobenzol.

The experience gained in making tribromtrinitrobenzol for the work described in this paper has led us to introduce into the process given in previous papers[3] from this Laboratory some improvements, which are described in this section.

To the preparation of tribromaniline we have nothing to add, but in the conversion of it into tribrombenzol we have found it best to proceed as follows: 50 grams of dry tribromaniline were dissolved with the aid of heat in 300 cc. of alcohol containing 75 cc. of benzol to increase its solvent power, and 20 cc. of common strong sulphuric acid added to the hot solution from a pipette. If this formed a precipitate, it was dissolved by longer heating, more of the solvents being added if necessary. 20 grams of

[1] It is a curious fact that even the melting-points are nearly the same.

[2] Ber. d. chem. Ges. **23**, 1344.

[3] This Journal **10**, 284; **12**, 9, 166.

finely powdered sodic nitrite were then sifted into the hot liquid, as rapidly as the violence of the action would permit; after which the whole was heated until the effervescence had ceased, and, after standing over night, filtered, washed, and dried, when the product could be treated directly with nitric acid to make the tribromdinitrobenzol in the manner already described.[1] The yield of tribrombenzol was good, 42–44 grams from the 50 grams of tribromaniline. The filtrate and washings contained so little of the organic substance that it was not worth while to work them up.

In the conversion of this body into tribromtrinitrobenzol we have found the cause of the much larger yield obtained by Dr. Moore[2] than by Dr. Wing.[3] This does not depend so much on the larger proportion of fuming sulphuric acid used, as on the rapidity with which the boiling is carried on. To get the best yield we found it necessary to raise the mixture to the boiling-point as quickly as possible, and to keep it boiling violently during the whole of the three hours. Under these conditions the yields varied from 8 to 10 grams of tribromtrinitrobenzol from 20 grams of tribromdinitrobenzol, that is, 36 to 45 per cent. of the theoretical, if both the nitric and fuming sulphuric acids were of the best quality. To prove that this violent boiling was the cause of the large yields, in one experiment the mixture was allowed to stand in the cold for a week, and then kept barely at the boiling-point for seven hours, when it yielded only 18 per cent. of the tribromtrinitrobenzol.

The Nitrite of Bromtrinitrophenylmalonic Ester, $C_6HBr(NO_2)_3.C.NO_2.(CO.OC_2H_5)_2$.

This substance was prepared as follows: 3 grams of bromtrinitrophenylmalonic ester[4] were mixed with about 10 grams of nitric acid, specific gravity 1.38, and warmed in a dish for three minutes on the water-bath, when both the undissolved organic substance and the acid became intense blood-red; the mixture was then allowed to cool, the acid liquid poured off, and the solid residue warmed once more for two minutes with about the same volume of fresh acid. After this the acid was decanted off, and the solid crystalline product washed with water till free from nitric acid, which changed it from a deep blood-red to a pale reddish-

[1] This Journal **12**, 166. [2] Ibid. **12**, 9. [3] Ibid. **10**, 285.
[4] Melting at 104° (This Journal **12**, 9.)

white color. The purification of this substance gave us much trouble at first on account of its slight stability, since even the short warming necessary to dissolve it in alcohol was sufficient to decompose it partially, while longer heating with alcohol produced complete decomposition; but at last we obtained satisfactory results from the following method: The crude substance, after the thorough washing with water mentioned above, was dissolved in warm chloroform, in which it is freely soluble, but even with this solvent care must be taken to warm the mixture for as short a time as possible; it was advisable, therefore, to achieve the solution rather by the use of a larger quantity of chloroform than by using a smaller volume at a higher temperature. This chloroform solution was then diluted with about its own volume of common alcohol, when the substance gradually separated in well formed white prisms, and was obtained pure after two of these crystallisations. It must be dried *in vacuo*, as it decomposes on the water-bath; in fact, even the temperature of a steam radiator (about 70°) was sufficient to bring about a partial decomposition.

A small additional amount of this substance could be obtained from the red nitric acid mother-liquors formed in its preparation, either by adding water or by evaporating them to dryness; but this quantity is so small that it is not worth the amount of work necessary to free it from the red viscous impurity with which it is mixed, especially as the mother-liquors can be used to more advantage for the preparation of the bromtrinitrophenyltartronic ester made by the longer action of hot nitric acid on bromtrinitrophenylmalonic ester.[1]

The same substance was formed when the bromtrinitrophenylmalonic ester stood in the cold with nitric acid of specific gravity 1.38 for three days. At first there was no visible change, but after two hours the mixture began to show a red color, which increased in intensity to a deep blood-red. The product was purified in the way just described, but this method of making it is on the whole not so good as that at a temperature of 100°.

The ease with which the substance breaks up under the influence of heat rendered the combustion of it a matter of great difficulty, since we encountered at one time an almost explosive

[1] On one occasion the acid mother-liquors yielded by spontaneous evaporation large white prisms, which melted in the crude state at about 99°, and were apparently somewhat soluble in water; but, although we have tried in many ways, we have not succeeded in obtaining this substance a second time.

evolution of gas, and at another the formation of a partial vacuum in the tube. The latter we are inclined to ascribe to the sudden absorption by the plumbic chromate of the large quantity of bromine given off by the substance. We finally succeeded in getting good results by spreading out the weighed portion through the whole length of a long porcelain boat, and then applying the heat so gradually that a layer of not more than a few millimeters of it melted at any one time. Care was also taken that the temperature did not rise much above 115° until the whole of the substance had been melted, after which the combustion was finished in the usual way without trouble.

The analyses led to the following results:

I. 0.2157 gram substance gave on combustion 0.2514 gram CO_2 and 0.0496 gram H_2O.

II. 0.1978 gram substance gave 0.2310 gram CO_2 and 0.0428 gram H_2O.

III. 0.1978 gram substance gave 0.2324 gram CO_2 and 0.0430 gram H_2O.

IV. 0.2014 gram substance gave 20.6 cc. nitrogen at a temperature of 24° and a pressure of 772.6 mm.

V. 0.1890 gram substance gave 18.6 cc. nitrogen at a temperature of 19° and a pressure of 752.8 mm.

VI. 0.2101 gram substance gave by the method of Carius 0.0813 gram AgBr.

VII. 0.2078 gram substance gave 0.0792 gram AgBr.

VIII. 0.2054 gram substance gave 0.0776 gram AgBr.

	Found.							
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Carbon	31.79	31.84	32.03	...	...	...	...	...
Hydrogen	2.56	2.40	2.42	...	...	...	...	...
Nitrogen	...	...	...	11.66	11.20	...	...	...
Bromine	...	...	...	...	...	16.47	16.22	16.08

These analytical results agree best with the percentages required by a substance formed from the bromtrinitrophenylmalonic ester by replacing one of its atoms of hydrogen by the radicle NO_2, as is seen from the following table:

	Calculated for $C_6HBr.(NO_2)_3.C.NO_2.(CO_2C_2H_5)_2$.	Found. Mean.
Carbon	31.52	31.88
Hydrogen	2.22	2.46
Nitrogen	11.32	11.43
Bromine	16.16	16.26

Our reasons for the position assigned to the radicle NO_2 in this formula, and for supposing that it is not a nitro group ($-N\equiv O_2$), but a nitrite group ($-O-N=O$), have been already stated in the introduction to this paper. The yield is satisfactory on the whole: 5 grams of bromtrinitrophenylmalonic ester gave 3.26 grams of the substance,[1] instead of the 5.5 grams required by the calculation, that is, 59 per cent. of the theoretical yield.

Properties of the Nitrite of Bromtrinitrophenylmalonic Ester. —It occurs usually in short, thick, well-developed, glistening white prisms, with terminations consisting of two planes at both ends, which seem to indicate that the crystals belong to the monoclinic system. Less commonly the prisms are long and rather slender, with terminations similar to those of the shorter form. Its behavior when heated is very characteristic. If a tube containing some of it is dipped into an oil-bath at 124°–126°, the substance turns red round the sides, then deeper, and the action gradually runs through the mass, until after a second or two the whole is melted, forming a dark blood-red liquid, which occupies many times the volume of the original substance, and contains bubbles of gas. The action is evidently a decomposition, and can be produced at much lower temperatures, since if the tube containing the substance, instead of being dipped into the heated bath as described above, is gradually heated with the bath, the action takes place even below 120°. In fact, it can also be brought about by long-continued heating in the steam-bath, or partially even at 70°. It is evident, therefore, that the compound has no definite melting- or decomposition-point, but yet the temperature given at first (124°–126°) can be used as such in purifying the substance, since it is essentially constant, if care is taken always to heat the samples examined in the same way.

This decomposition seemed so interesting that we examined it more carefully. For this purpose a considerable quantity of the nitrite of bromtrinitrophenylmalonic ester was heated in a test-tube inserted in an air-bath, and the gaseous products of the reaction drawn through a solution of baric hydrate. At 103°–108° there was a quantity of red vapor given off, and a precipitate of baric carbonate formed in the tubes containing the baric hydrate solution. The red vapor was recognised by the smell as bromine,

[1] In addition to this amount 0.7 gram of bromtrinitrophenyltartronic ester was obtained from the mother-liquors.

and this was confirmed by the precipitation of argentic bromide when argentic nitrate was added to the acidified filtrate from the baric carbonate. On the other hand, we could not detect a trace of nitrate or nitrite with ferrous sulphate and sulphuric acid. After the substance had been heated to 103°–108° for three hours, the temperature was raised to 125° for two hours and a half, but the additional loss at this higher temperature was very small. We intended originally to determine quantitatively the amounts of the various products, but abandoned this idea when we found that the loss was not constant, three experiments giving 25 per cent., 30 per cent., and 21 per cent., respectively. The appearance of the bromine, too, shows that there has been a complete decomposition of a part of the substance, and therefore the volatile products are of so little interest that we did not care to spend the time necessary for the identification of the others, which must have been formed in addition to the bromine and carbonic dioxide. On the other hand, we were much interested in the non-volatile product of the reaction left in the test-tube as a fused, rather viscous mass of a brownish red color, in which crystals were imbedded. It was purified by washing several times with alcohol, which removed much of the viscous portions; then the residue was crystallised, first from dilute, and finally from common alcohol, and when pure showed the melting-point 156° and the crystalline form of the bromtrinitrophenyltartronic ester described later in this paper. The action of heat on our nitrite, therefore, is similar to the well-known conversion of the so-called nitrotartaric acid into tartronic acid.

The nitrite of bromtrinitrophenylmalonic ester is almost insoluble in cold water, perhaps a little more soluble in boiling water; but if the substance was boiled for some time with water, the crystals were converted superficially into a dark red, oily substance, and the water gave a slight test for bromine; this decomposition seemed to be due, however, only to the heat (see above), not to the presence of the water. It is slightly soluble in cold, more freely in hot ethyl alcohol, but this solution is easily decomposed by heat, since boiling for fifteen minutes converts the substance completely into a brownish red, viscous product, resembling half-dried varnish, from which nothing definite could be isolated, and even a very short heating with alcohol is sufficient to form some of this viscous body. Its solubility in methyl alcohol resembles

that in ethyl alcohol; it is freely soluble in chloroform or acetone; soluble in benzol or glacial acetic acid; slightly soluble in carbonic disulphide; very slightly in ether, and essentially insoluble in ligroine. The best solvent for it is the mixture of chloroform and alcohol described above. Strong sulphuric acid seems to have no action on it in the cold, or if heated, until the substance decomposes, when it dissolves, forming a reddish solution; strong hydrochloric acid has no action on it, either hot or cold, as long as the substance does not decompose; strong nitric acid has little or no action on it in the cold, even when allowed to stand with it for some weeks; when heated to 100° it converts it gradually into the bromtrinitrophenyltartronic ester, as is described in detail later in this paper under the preparation of that substance.

Ammonic hydrate acts on it little, if at all, even when the action is assisted by the addition of alcohol; sodic hydrate in aqueous solution has no action, but if alcohol is added the crystals begin to dissolve slowly, imparting a red color to the liquid, but only a partial solution is effected in the cold. From this observation we inferred that no salt was formed until the nitrite was decomposed, and to test the accuracy of this inference we treated some of the nitrite with an alcoholic solution of sodic ethylate, which gave at once a dark blood-red coloration; but even here only a part, and that not the larger part, of the crystals of the nitrite was dissolved; the red solution poured off from the unaltered crystals gave a good test for a nitrite with starch paste, potassic iodide, and dilute sulphuric acid, with ferrous sulphate and sulphuric acid, and by Liebermann's reaction, so that there can be no doubt that sodic nitrite was formed in the experiment. This proves the correctness of our inference that the substance melting at 124°–126° cannot form salts; and the blood-red salt observed must have been derived from the decomposition-product left after the removal of the group NO_2 from our substance. It may be added that acid or neutral sodic carbonate has no action on the nitrite in aqueous solution, and very little, if any, in presence of alcohol.

Nitrite of Anilidotrinitrophenylmalonic Ester,
$C_6H(C_6H_5NH).(NO_2)_3.C.NO_2.(CO.OC_2H_5)_2$.

Aniline acts with great violence on the nitrite of bromtrinitrophenylmalonic ester. If the substances are mixed at ordinary temperatures, the action is almost explosive, a good part of the

mixture is thrown out of the beaker, and the product seems to be principally carbon. If the mixture is kept cool by immersing the beaker in water, the action goes more mildly, but the product is still very black and impure. We therefore carried on the reaction in ethereal solution with the best results as follows: 1 gram of the nitrite of bromtrinitrophenylmalonic ester was mixed with a small quantity of ether, and, disregarding the fact that a portion of the crystals had not dissolved, a slight excess of aniline was added; the ether at once turned red, and the undissolved crystals of the nitrite were taken up, while aniline bromide was deposited in their place. At the end of a few minutes the reaction was complete, and, after washing out the aniline and aniline bromide with water containing a little hydrochloric acid, the ether was allowed to evaporate, when it left a vivid red mass, which was purified by dissolving it in hot chloroform, avoiding long heating, and then adding alcohol until the crystals began to separate, as it had been found that this substance, like the corresponding bromine-compound, was decomposed by heating with alcohol. After the substance showed the constant melting-point 119° it was dried *in vacuo* for analysis.

The combustion of this substance was even more difficult than that of the bromine-compound, as it decomposed with almost explosive violence at a temperature a few degrees above its melting-point, and did not begin to decompose at all at lower temperatures. We were unable therefore to burn it in an open tube, but at last got satisfactory results by using a closed tube, mixing it with a long layer of plumbic chromate and applying the heat very gradually. Its analyses led to the following results:

I. 0.1542 gram substance gave on combustion 0.2538 gram CO_2 and 0.0678 gram H_2O.

II. 0.1494 gram substance gave 18.9 cc. nitrogen at a temperature of 24.3° and a pressure of 752.3 mm.

	Calculated for $C_6H(C_6H_5NH).(NO_2)_3.C.NO_2.(CO_2C_2H_5)_2$.	Found. I.	Found. II.
Carbon	44.97	44.88	...
Hydrogen	3.35	4.88	...
Nitrogen	13.80	...	14.02

In spite of the unsatisfactory number for the hydrogen, these results prove that the substance has the formula which we have assigned to it. The yield was good, 0.9 gram of the nitrite of the

bromtrinitrophenylmalonic ester giving 0.7 gram of the anilido-compound, instead of the 0.92 gram required by the theory, that is, 76 per cent.

Properties.—The nitrite of the anilidotrinitrophenylmalonic ester is a very beautiful substance, crystallising in rhombohedra often two millimeters long and one millimeter thick, with a very acute angle, which is frequently, but not always, truncated by a basal plane. The color of the crystals by reflected light is a rich full red, somewhat darker than that of chromic anhydride; by transmitted light, orange-red. It melts at 119°, turning black and giving off a few bubbles of gas, if the temperature has not risen above this point; but at 120° it decomposes with such violence that frequently a good part of the substance is thrown out of the capillary melting-tube. It is essentially insoluble in cold water, and its solubility does not seem to be increased by heat; very slightly soluble in cold ethyl alcohol, more soluble in hot, but still not freely, the hot solution seems to undergo partial decomposition; more soluble in methyl alcohol, whether cold or hot, than in ethyl alcohol, but not freely even in this; very freely soluble in chloroform; freely in benzol or acetone; soluble in glacial acetic acid; slightly in ether or carbonic disulphide; insoluble in ligroine. The best solvent for it is a mixture of chloroform and alcohol. Strong sulphuric acid seems not to act on it in the cold, but when heated with it the substance decomposes, and then dissolves with a blackish color; strong nitric acid does not act on it in the cold, but when hot dissolves it with a yellow color; strong hydrochloric acid has no action on it, whether cold or hot.

The nitrite of anilidotrinitrophenylmalonic ester showed marked acid properties. Acid sodic carbonate in aqueous solution had no action with it, but, if assisted with alcohol, gave a red solution; potassic carbonate behaved in the same way; sodic hydrate turned the crystals black, forming at the same time a brownish solution, which on addition of alcohol became deeper and blackish red, turning in time to blackish brown; ammonic hydrate in aqueous solution gave a red color, but the action was not complete until alcohol was added, when a very dark red solution was formed. The nitrite of anilidotrinitrophenylmalonic ester therefore shows much more acid properties than the corresponding bromine-compound, which is indifferent to all these reagents except sodic hydrate in presence of alcohol, and this fact puzzled

us at first, until we decided that the hydrogen attached to the nitrogen in the anilido radicle (C_6H_5NH) might be rendered acid by the presence of the three nitro groups. That this is the correct explanation of the phenomenon we have proved by preparing and analysing the sodium salt of anilidotrinitrotoluol, which contains no atom of hydrogen that could be replaced by sodium except the one attached to the nitrogen of the aniline radicle. The description of this work will be found in the following section.

An attempt to analyse the sodium salt of the nitrite of anilidotrinitrophenylmalonic ester gave no satisfactory result, owing undoubtedly to the partial formation of sodic nitrite from the organic nitrite by the action of the sodic hydrate used in making the salt.

Sodium Salt of Anilidotrinitrotoluol,

$C_6.CH_2.H.(C_6H_5NNa).(NO_2)_2$.

To prepare this salt, 1 gram of anilidotrinitrotoluol[1] (melting-point 151°) was dissolved in alcohol, and mixed with an alcoholic solution of 0.09 gram of sodic hydrate, that is, over 0.03 gram less than the amount required to convert the gram of substance into its salt; a little ether was then added, and the solution of the salt evaporated rapidly to dryness in a narrow beaker sunk throughout its whole length in the steam-bath. During the evaporation there was an odor of phenyl isocyanide. The dry mass was washed thoroughly with benzol to remove the excess of anilidotrinitrotoluol, the residue dried at 100°, and analysed. As the salt explodes when heated with strong sulphuric acid, it should be dissolved in water, treated with dilute sulphuric acid, filtered, and the filtrate evaporated to dryness and converted into neutral sodic sulphate.

0.7876 gram salt gave 0.1662 gram Na_2SO_4.

	Calculated for $C_6.CH_2.H.(C_6H_5NNa).(NO_2)_2$.	Found
Sodium	6.76	6.84

The salt prepared as described above forms a maroon-black powder, which explodes gently when heated alone, or with strong sulphuric acid, forming in the latter case a very loose, spongy, blackish mass. It is soluble in alcohol with a yellowish brown color like that of ferric chloride; insoluble in ether or benzol; water decomposes the salt almost completely, forming a yellow

[1] This Journal **12**, 6.

precipitate and a pale brown solution, which is strongly alkaline. The action of the anilidotrinitrotoluol with alkaline reagents was also studied, and, as was to be expected, no action was obtained with acid or neutral carbonate of sodium, or ammonic hydrate in aqueous solutions; but if the action was assisted by the presence of alcohol, each of these reagents gave a barely perceptible reddish coloration, so slight in the case of ammonic hydrate that we were doubtful whether there had been any action; sodic hydrate in aqueous solution gave a slight yellow coloration, which, on the addition of alcohol, was at once converted into a very dark blood-red. The acid character of the anilidotrinitrotoluol therefore is much less marked than that of the nitrite of anilidotrinitrophenylmalonic ester, and as the position of the anilido group with regard to the nitro groups is the same in both compounds, we must ascribe this to the presence of the nitrite of the malonic-ester radicle $C.NO_2.(CO.OC_2H_5)_2$, with its large amount of oxygen in place of the indifferent methyl contained in the toluol.

Bromtrinitrophenyltartronic Ester,
$C_6HBr.(NO_2)_3.C.OH.(CO.OC_2H_5)_2$.

If the nitrite of bromtrinitrophenylmalonic ester, or the ester itself, was heated for some time with nitric acid, it was converted into the corresponding tartronic ester, which we found it convenient to prepare as follows: 1 gram of bromtrinitrophenylmalonic ester was mixed with about 10 cc. of nitric acid of specific gravity 1.38, and heated on the water-bath for three hours in a dish covered with a watch-glass, fresh nitric acid being added when necessary to replace that lost by evaporation. At the end of this time the substance was found to be completely dissolved in the small quantity of hot nitric acid left, but upon cooling colorless crystals separated, which, after washing with water, were essentially the pure substance, one recrystallisation from alcohol being all that was needed to make them melt at 156°, the constant melting-point of this compound. If, as was usually the case, the bromtrinitrophenylmalonic ester was contaminated with acetylenetetracarbonic ester, a yellowish oil was also formed, which, however, remained dissolved in the nitric acid mother-liquor. The amount of the substituted tartronic ester in this mother-liquor was so small that it did not pay for the working up.

The bromtrinitrophenyltartronic ester can also be made from

the nitrite of the corresponding malonic ester, but this method has no advantage over the preparation direct from the malonic ester described above, except in the case of the nitric acid mother-liquors from making the nitrite, which yield on longer heating with nitric acid a small amount of the tartronic ester, and this is worth saving on account of the tedious and costly preparation of the mother-substance.

The substance dried *in vacuo* was analysed with the following results:

I. 0.1951 gram substance gave on combustion 0.2380 gram CO_2 and 0.0584 gram H_2O.

II. 0.2049 gram substance gave 16.2 cc. nitrogen at a temperature of 17.5° and a pressure of 763.7 mm.

III. 0.2044 gram substance gave according to the method of Carius 0.0836 gram AgBr.

IV. 0.2272 gram substance gave 0.0930 gram AgBr.

	Calculated for $C_6HBr.(NO_2)_3.C.OH.(CO_2C_2H_5)_2$.	Found. I.	II.	III.	IV.
Carbon	33.47	33.28	...	...	...
Hydrogen	2.58	3.33	...	...	...
Nitrogen	9.02	...	9.20	...	...
Bromine	17.17	...	...	17.41	17.42

Our reasons for considering this a tartronic ester rather than a phenol have been given already in the introduction to this paper. The yield is satisfactory, considering the amount of loss to be expected from such a method of preparation: 1 gram of bromtrinitrophenylmalonic ester gave 0.4 gram of the substance, or about 40 per cent. of the theoretical yield.

Properties.—The bromtrinitrophenyltartronic ester crystallises from alcohol in long white prisms, terminated by planes at a very obtuse angle to each other, so that the ends look almost but not quite square. These crystals are often arranged in radiating groups, and in that case are generally much more slender than when occurring in isolated prisms. It is deposited from its solution in hot nitric acid in rather sharp slender needles. It melts at 156°, and is nearly but not quite insoluble in water, whether hot or cold; soluble in cold alcohol, freely in hot; rather more soluble in methyl than in ethyl alcohol; freely soluble in benzol, glacial acetic acid, or acetone; soluble in ether, and somewhat more so in chloroform; nearly insoluble in carbonic disulphide; insoluble

in ligroine. The best solvent for it is hot alcohol. Strong sulphuric acid has no action upon it in the cold, but if hot dissolves it with difficulty with a reddish brown color; strong hydrochloric acid has no action on it, hot or cold, in open vessels, but decomposes it if the two substances are heated together in a sealed tube; nothing could be obtained from the products, however, except a mass like a dry varnish, which we did not succeed in bringing into a state fit for analysis. An exactly similar result was obtained in an attempt to saponify it with sulphuric acid of specific gravity 1.44. Strong nitric acid has no action on it at first, whether cold or hot, but if heated with it for some time seems to destroy it completely, and a similar result was obtained upon boiling it with bromine and water, as in both these cases we could not succeed in isolating any organic oxidation product.

Acid sodic carbonate in aqueous solution had no action on bromtrinitrophenyltartronic ester, but on the addition of alcohol a pale red color appeared, which became more marked on standing; potassic carbonate also did not affect it in aqueous solution, but gave a strong dark red solution on addition of alcohol; aqueous sodic hydrate turned the crystals brown, and dissolved some of them with a brownish color; on the addition of alcohol all the substance went into solution with a dark red color; ammonic hydrate gave a red solution, but the action was not complete until alcohol was added, when the solution became very dark red. The bromtrinitrophenyltartronic ester therefore showed the strong acid character which we should expect, but no attempt was made to analyse its salts, as it was found that the bromine atom was removed by alkaline solutions with great ease, sodic bromide being formed when it was treated with sodic ethylate, even in the cold.

Anilidotrinitrophenyltartronic Ester,

$C_6H.(C_6H_4NH).(NO_2)_2.C.OH.(CO.OC_2H_5)_2$.

This substance was made by adding an excess of aniline to solid bromtrinitrophenyltartronic ester; the reaction ran smoothly with a slight evolution of heat, and was complete after the mixture had been allowed to stand for a few minutes, when the aniline bromide and excess of aniline were removed by washing with very dilute hydrochloric acid, and the bright yellow residue purified by crystallisation from alcohol. At first rounded masses of radiating needles looking like little balls of fat of a bright yellow color

were obtained, but as the crystallisation continued, orange-red prisms began to appear, and increased in quantity until after several recrystallisations the greater part of the substance had been converted into this form. This behavior during crystallisation suggested to us that the substance probably occurred in two modifications, which was proved to be the case by the determination of the melting-points of the two sorts of crystals, the yellow, after thorough purification, melting at about 122°, the red at 143°. As the substance passes from one form to the other with great ease, many experiments were necessary in order to find methods for obtaining each in a state of purity.

Red Modification of Anilidotrinitrophenyltartronic Ester.

To obtain this form from the crude product of the reaction it was crystallised several times from alcohol, until a mixture of the two forms rich in red had been obtained, and then a strong alcoholic solution of the mixed crystals was allowed to evaporate slowly at temperatures from 50° to 70°. The product thus obtained, which showed no sign of the yellow form, was dried at 100°, and analysed with the following results:

I. 0.1792 gram substance gave on combustion 0.3114 gram CO_2 and 0.0694 gram H_2O.

II. 0.2016 gram substance gave on combustion 0.3534 gram CO_2 and 0.0809 gram H_2O.

III. 0.1938 gram substance gave 19.9 cc. nitrogen at a temperature of 22° and a pressure of 767.7 mm.

	Calculated for $C_6H.(C_6H_3NH).(NO_2)_3.C.OH.(CO_2C_2H_5)_2$.	Found. I.	II.	III.
Carbon	47.69	47.40	47.80	...
Hydrogen	3.77	4.30	4.46	...
Nitrogen	11.71	...	...	11.76

The air-dried red crystals lost only 0.19 per cent. when dried at 100°, and therefore were free from water or alcohol of crystallisation.

Properties.—The red form of anilidotrinitrophenyltartronic ester crystallises in well formed prisms, often half a centimeter long, with at each end a pyramidal termination consisting of four planes. It has an orange-red color like that of potassic dichromate, and melts at 143°; is essentially insoluble in cold water, very slightly soluble in boiling water, forming a pale yellowish solution; soluble

in cold alcohol, rather freely in hot. This solution if allowed to evaporate at temperatures from 50° to 70° deposits crystals of the red modification, as has been already stated; but if allowed to evaporate at ordinary temperatures, a mixture of red and yellow crystals is usually obtained, although occasionally only red crystals are formed under these conditions. The red modification is more soluble in methyl than ethyl alcohol; very freely in acetone. Both these solutions deposit some yellow crystals. Soluble in ether or chloroform; slightly soluble in cold benzol, freely in hot. The solution in benzol or chloroform deposits the substance in a viscous state. It is slightly soluble in cold glacial acetic acid, more soluble in hot; from this solution it is precipitated by the addition of water, usually in the yellow form, although once or twice we thought we obtained the red modification; very slightly soluble in carbonic disulphide; insoluble in ligroine. Strong sulphuric acid when cold has no action on it, but dissolves it with a brownish yellow color when hot; strong nitric acid dissolves it partially when cold with a yellow color, and the action is increased by heating; cold hydrochloric acid has no action on it, but dissolves it very slightly when hot.

Yellow Modification of Anilidotrinitrophenyltartronic Ester.

This substance was most conveniently obtained from the mixture of the two forms after it had been purified by several crystallisations from alcohol, by dissolving it in warm glacial acetic acid, and, after allowing the solution to stand for some hours, precipitating the solid matter by the addition of water. The yellow powder thus obtained was dried at ordinary temperatures over sulphuric acid, and anlysed with the following results:

I. 0.1879 gram substance gave on combustion 0.3284 gram CO_2 and 0.0726 gram H_2O.

II. 0.1924 gram substance gave 20.5 cc. nitrogen at a temperature of 25° and a pressure of 769.7 mm.

	Calculated for $C_6H.(C_6H_4NH).(NO_2)_3.C.OH.(CO_2C_2H_5)_2$.	Found. I.	II.
Carbon	47.69	47.66	...
Hydrogen	3.77	4.29	...
Nitrogen	11.71	...	12.05

The substance dried over sulphuric acid lost no weight when heated to 100°, showing that it contains neither water nor alcohol of crystallisation.

Properties.—The yellow form crystallises in very fine needles united into spherical groups like those of wavellite, looking frequently like little balls of fat, and has a full yellow color like that of potassic chromate. It is hard to determine the melting-point with accuracy, because this form is quickly changed into the red modification, at least in part, when heated to a few degrees below that temperature; it is necessary therefore to heat the bath up to the melting-point before immersing the capillary tube containing the substance; under these conditions it melts, and then changes to the red form, and solidifies again, after which it does not melt until about 140°. The melting-point we ascribe to this substance is 122°, but we are not sure that this is accurate to one degree. This change from yellow to red can also be brought about slowly by heating at 100°, by boiling the yellow form with water for some time, or, most conveniently, by crystallisation from alcohol at temperatures from 50° to 70°. In its solubility in the different solvents the yellow form does not differ much from the red, but seems in general to be more soluble.

We have made many attempts to determine the molecular weights of the two modifications by the method of Raoult, but have not as yet succeeded in finding any solvent which gives satisfactory results. Acetic acid, owing to its conversion of the red into the yellow form, could at best give results only for the latter, but a number of determinations showed us that it was of no use even for this purpose, as results were obtained varying from 295 to 345 (the theoretical molecular weight is 478), therefore showing that some reaction (probably the formation of an acetoxymalonic ester) had taken place between the acetic acid and the ester. An experiment with phenol gave an excellent result with the red form, 477 instead of 478; but with the yellow only 307 was obtained, indicating a chemical action similar to that observed with acetic acid, and we are not inclined to accept any result with phenol, however excellent it may appear, as with a substance which is so easily affected by solution as this there can be no certainty that it has remained in the same modification, unless it can be recovered directly from the solution used, and this we have found no means of doing in the case of phenol. Benzol gives such uncertain results with substances containing a hydroxyl group,[1] that we did not think it worth while to try it. We have

[1] Ber. d. chem. Ges. **21**, 707.

hopes that naphthaline[1] may give the desired result for the red form; this will be tried in this laboratory, and a further attempt made to find a satisfactory solvent for the yellow modification; but as the departure of one of us from Cambridge makes it necessary to postpone further work in this direction until next year, we have thought it best to publish at once our present results, which have already reached a certain completeness.

Salts of Anilidotrinitrotartronic Ester.

The anilidotrinitrotartronic ester has well marked acid properties. An aqueous solution of acid sodic carbonate has essentially no action on it, but if alcohol is added there is a slight but distinct action indicated by the change of color; potassic carbonate gives in aqueous solution a slight red color, which becomes a strong red if alcohol is added; sodic hydrate in aqueous solution gives a very dark red, apparently converting the substance completely into its salt; ammonic hydrate also gives a strong red color, which is intensified on the addition of alcohol. Some of the alkaline salts were studied more carefully with the following results:

Monopotassium Salt, $C_6H.(C_6H_5NH).(NO_2)_3.C.OK.(CO.OC_2H_5)_2$.

This salt was made by adding 20 cc. of absolute alcohol to 0.5 gram of the ester, and then a large excess of pure potassic carbonate; carbonic dioxide was given off, the solution became very dark red, and after digesting the substances for eight to ten minutes with the occasional aid of a little heat, the dark brown solution was filtered from the excess of potassic carbonate, evaporated to dryness in a beaker sunk throughout its whole length in the steam-bath, and analysed with the following results:

I. 0.3458 gram salt, heated with strong sulphuric acid, gave 0.0548 gram K_2SO_4.

II. 0.3748 gram salt gave 0.0696 gram K_2SO_4.

	Calculated for $C_6H.(C_6H_5NH).(NO_2)_3.C.OK.(CO_2C_2H_5)_2$.	Found. I.	II.
Potassium	7.58	7.11	8.34

The absolute alcohol used in the second analysis had not been freshly prepared, and the slight excess of potassium can be accounted for by the assumption that it had absorbed a little water.

[1] Ber. d. chem. Ges. **23**, Ref. 128.

Properties.—The acid potassic anilidotrinitrophenyltartronic ester, when prepared by the method described above, forms a brownish-black amorphous solid, freely soluble in water or alcohol, slightly soluble in ether, and insoluble in benzol. The solutions have a dark brown color.

Disodium Salt, $C_6H.(C_6H_5NNa).(NO_2)_2.C.ONa.(CO.OC_2H_5)_2$.

This salt seemed to be formed, to our great surprise, by the action of an alcoholic solution of sodic hydrate on an excess of the anilidotrinitrophenyltartronic ester. To prepare it, about 0.7 gram of the ester was mixed with a little alcohol, and somewhat less than the amount of sodic hydrate (also in alcoholic solution) necessary to form a mono-sodium salt; a little ether was then added to the dark red solution, which was evaporated rapidly to dryness, the small beaker containing it being sunk throughout its length in the steam-bath. After this the excess of unaltered ester was extracted with benzol, and the salt dried at 100°, and analysed with the following results:

I. 0.2596 gram salt gave after evaporation and ignition with sulphuric acid, 0.0672 gram Na_2SO_4.

II. 0.2848 gram salt gave 0.0698 gram Na_2SO_4.

	Calculated for $C_6H.(C_6H_5NNa).(NO_2)_2.C.ONa.(CO_2C_2H_5)_2$.	Found. I.	II.
Sodium	8.81	8.39	7.94

These results agree with the percentage corresponding to the formula as nearly as can be expected, when it is remembered that the salt was not crystallised, or purified in any other way; but still we cannot feel that they do more than make it highly probable that this is the composition of the salt, as it is certainly strange that a neutral salt should have been formed when such an excess of the acid substance was present, and we had no means of proving that the substance analysed was a pure salt rather than a mixture; in fact, we observed a slight smell of phenyl isocyanide during its preparation, indicating a deep decomposition of part of it, —only a very small part, however, if we may judge from the smell.

Properties.—The salt prepared as described above formed a dark reddish brown to black amorphous mass, soluble in water or alcohol; slightly soluble in ether; insoluble in benzol. Its solutions have a brownish red color.

The behavior of a solution of the ammonium salt of anilidotrinitrophenyltartronic ester, made by adding ammonic hydrate to an excess of the ester, although it smelt strongly of ammonia, was tested with various reagents and gave the following characteristic precipitates:—

With a *zinc salt*, orange-brown.

With a *manganese salt*, brown.

With a *cadmium salt*, reddish brown.

With a *copper salt*, yellowish brown.

With a *lead*, *mercuric* or *silver salt*, reddish brown.

The fact that the ammonium salt gives no precipitate with salts of magnesium, calcium, strontium or barium, is also highly characteristic.

Although, as has been already stated, no definite results were obtained from our attempts to oxidise or saponify the bromtrinitrophenyltartronic ester, we thought that perhaps the anilido-compound might behave better, and accordingly the following experiments were made, in the hope (unfortunately not realised) of decomposing the anilidotrinitrophenyltartronic ester into substances which would confirm our inferences in regard to its nature. The substance was allowed to stand in the cold with an aqueous solution of potassic permanganate, but, although a considerable part of it disappeared, no organic oxidation product could be detected. In the hope of saponifying the ester, we added to it an excess of sodic hydrate dissolved in water, and allowed the reddish brown solution thus formed to stand in a corked flask at ordinary temperatures for some weeks. During this standing a strong odor of phenyl isocyanide was developed, and, if the amount of ester was small, the color changed to yellow; if, on the other hand, the quantity was large, it retained its dark brown color; at the end of the experiment, nothing was obtained except a brown precipitate of most unpromising appearance, formed by adding an acid to the solution, and the phenyl isocyanide already mentioned as recognised by its smell. As the formation of this substance would necessitate a complete destruction of the benzol ring which carried the nitro groups and malonic-ester radicle, we did not think it worth while to repeat the experiment.

This formation of an isocyanide from the destruction of a benzol ring containing nitro groups by means of an aqueous solution of sodic hydrate recalls the work of Post and Hübner,[1] who found

[1] Ber. d. chem. Ges. **5**, 408.

that ordinary dinitrobenzol when boiled with a solution of sodic or potassic hydrate was decomposed with formation of a cyanide, quickly if the solution was strong, slowly if it was dilute. They also found that picric acid behaved in the same way, thus confirming the earlier observation of Wöhler.[1]

Anilidotrinitrophenylmalonic Ester,
$C_6H.(C_6H_5NH).(NO_2)_3.CH(CO.OC_2H_5)_2$.

This substance was made to see whether it would be possible by treatment with nitric acid to convert it directly into either its nitrite or the anilidotartronic ester described above. It was found, however, that standing for several days at ordinary temperatures with strong nitric acid produced complete decomposition of part of the substance, the only product insoluble in the acid being unaltered anilidotrinitrophenylmalonic ester; and that upon heating it on the steam-bath with nitric acid for three hours in the hope of making the anilidotrinitrophenyltartronic ester, the substance was destroyed completely, oxalic acid being the only product which we could find. It seems therefore that the less acid anilido-compound cannot be converted into the nitrite or tartronic ester. But although these attempts to oxidise the substance have failed, we add the description of the anilidotrinitrophenylmalonic ester, which has not been prepared heretofore.

It is easily made by adding an excess of aniline to solid bromtrinitrophenylmalonic ester. The reaction ran smoothly in the cold with slight evolution of heat, and the product was purified by washing with very dilute hydrochloric acid to remove the excess of aniline and the aniline bromide, and crystallisation from alcohol until it showed the constant melting-point 133°, when, after drying at 100°, it was analysed with the following result:

0.1866 gram substance gave 20.2 cc. nitrogen at a temperature of 25.5° and a pressure of 764.3 mm.

	Calculated for $C_6H.(C_6H_5NH).(NO_2)_3.CH(CO_2C_2H_5)_2$.	Found.
Nitrogen	12.13	12.12

Properties.—The anilidotrinitrophenylmalonic ester crystallises in long, slender, sharp needles arranged in radiating bunches. It has a full yellow color, and melts at 133°. It is very slightly, if at all, soluble in cold water, more soluble in hot, as shown by

[1] Ann. der Phys. Pogg. **13**, 488.

the faint yellow color of the solution; freely soluble in hot alcohol, less so in cold; somewhat more soluble in methyl than in ethyl alcohol; very freely soluble in chloroform; freely in benzol or acetone; soluble in ether, or glacial acetic acid; slightly in carbonic disulphide; insoluble in ligroine. Boiling alcohol is the best solvent for it. Strong sulphuric acid or nitric acid dissolves it slightly in the cold with a yellow color; the solubility is somewhat increased by heating; strong hydrochloric acid acts on it only very slightly, cold or hot. An aqueous solution of acid sodic carbonate has no action upon it, but there is a barely perceptible change of color if alcohol is added; aqueous potassic carbonate gives little if any action, but on the addition of alcohol a brown solution is formed; the action, however, seems to be incomplete; aqueous sodic hydrate turns the crystals dark and brown, the solution becoming yellow; the addition of alcohol seems to convert the substance completely into the sodium salt; aqueous ammonic hydrate gives a barely perceptible yellow color, which is not increased by the addition of a little alcohol, but a large amount gives a dark brown solution.

A solution of the sodium salt of anilidotrinitrophenylmalonic ester, made by adding a drop of sodic hydrate to an excess of the ester moistened with alcohol and then diluting largely with water, gave characteristic precipitates with the following reagents:

With a *calcium salt*, a heavy reddish brown precipitate.

With a *strontium salt*, a slighter precipitate.

With a *barium salt*, a very faint precipitate.

A *magnesium salt* gives a reddish brown precipitate, as heavy as that obtained with the calcium salt.

With a *manganese salt*, reddish brown flocks.

With a *zinc salt*, yellowish brown.

With a *cadmium salt*, orange-yellow.

With a *copper salt*, yellowish brown.

With a *lead salt*, reddish brown.

With a *silver salt*, dark reddish brown.

Its most striking property is that the barium salt is the most, the calcium salt the least, soluble of its salts with metals of the second group, and in this respect it resembles its mother-substance, the bromtrinitrophenylmalonic ester,[1] the corresponding acetacetic ester,[2] and the orthonitrobenzoylmalonic ester of Bischoff.[3]

[1] This Journal **12**, 12. [2] Ibid. **12**, 172. [3] Ann. Chem. (Liebig) **251**, 362.

Nitrite of Trinitrophenylenedimalonic Ester,
$C_6H.(NO_2)_3.CH(CO.OC_2H_5)_2.C.NO_2.(CO.OC_2H_5)_2$.

After we had studied the action of nitric acid on the bromtrinitrophenylmalonic ester, it seemed of interest to determine whether the dimalonic-compound acted in the same way, and accordingly we proceeded as follows: A small quantity of the trinitrophenylenedimalonic ester[1] (melting-point 123°) was covered with nitric acid of specific gravity 1.38 and warmed in a dish on the steam-bath for two minutes; the solid turned dark yellow, and melted to a drop of oil. The acid was then allowed to cool, poured off, and replaced by the same quantity of fresh acid, when it was warmed as before for three minutes, making five in all. Upon standing, the oily product solidified to a mass of crystals, which were washed thoroughly with water, and at first recrystallised from alcohol; but as in each crystallisation a small quantity of yellow oil was formed, we feared a partial decomposition, and resorted to the method which had given excellent results in the purification of the nitrite of bromtrinitrophenylmalonic ester, that is, dissolving the substance with very little heat in chloroform, and then adding enough alcohol to start the separation of crystals; in this way a pure substance melting at 111° was obtained without difficulty, which was dried at about 70° and analysed with the following results:

I. 0.1960 gram substance gave on combustion 0.3012 gram CO_2 and 0.0714 gram H_2O.

II. 0.1926 gram substance gave 16.7 cc. nitrogen at a temperature of 23° and a pressure of 771 mm.

	Calculated for $C_6H.(NO_2)_3.CH(CO_2C_2H_5)_2.C.NO_2.(CO^2C_2H_5)_2$.	Found. I.	II.
Carbon	41.81	41.91	...
Hydrogen	3.83	4.05	...
Nitrogen	9.76	...	9.93

The substance is therefore the mononitrite of trinitrophenylenedimalonic ester.

Properties.—The substance crystallises in rather thick plates with parallel sides terminated at each end by two planes at an acute angle to each other, these acute angles being usually, but not always, truncated by planes at right angles to the parallel sides. The crystals are often much twinned and grouped into very

[1] This Journal **12**, 20.

irregular forms. It has a lemon yellow color, and melts without decomposition at 111°. It is very slightly soluble in boiling water, giving a pale yellow solution, essentially insoluble in cold; slightly soluble in cold alcohol, freely in hot; more soluble in methyl than in ethyl alcohol, whether cold or hot; both these solvents seem to produce a slight decomposition of the substance when heated with it; very freely soluble in chloroform; freely soluble in benzol or acetone; soluble in ether or glacial acetic acid; slightly soluble in carbonic disulphide; insoluble in ligroine. The best solvent for it is the mixture of chloroform and alcohol used as described above. Strong sulphuric acid has no action on it in the cold, but when heated with it dissolves some of it with a pale yellow color after it melts; strong hydrochloric acid has no apparent action on it, either hot or cold; strong nitric acid has no action on it in the cold, but dissolves it slightly when hot, and if heated with it for two hours and a half destroys it completely, the only product which we isolated being oxalic acid; on one occasion, however, another product melting near 140° was obtained in small quantity, but we did not feel sufficiently interested in this part of the subject to prepare enough of it to determine whether it was the dinitrite or a tartronic ester. One thing, however, these experiments have established, namely, that the dimalonic-compound is less stable toward nitric acid than the brommalonic-compound, since the latter, after three hours' boiling with the acid, had not gone further than the tartronic ester, while the former usually underwent a total decomposition. On the other hand, the nitrite of the dimalonic-compound is not decomposed by melting, and only slightly by heating with alcohol, and therefore in these two respects is more stable than the nitrite of bromtrinitrophenylmalonic ester.

The nitrite of trinitrophenylenedimalonic ester shows acid properties. With an aqueous solution of sodic carbonate it gives no action, and very little when alcohol is added, unless in very large quantity, when a yellowish solution is formed; with potassic carbonate in aqueous solution there is no action, but on the addition of alcohol a very strong yellowish brown color; aqueous sodic hydrate gives a reddish solution, on the addition of alcohol an orange flame-colored solution, entirely different in color from that given with the potassic carbonate; ammonic hydrate imparts a strong yellow coloration to the solution, intensified on the addition of alcohol. Upon comparing the acidity of this substance

with that of the trinitrophenylenedimalonic ester, it seems as if this latter substance were somewhat more acid than the nitrite, since it gives a slight coloration with aqueous potassic carbonate and seems to act more easily with acid sodic carbonate and alcohol, but the difference between the two in this respect is certainly very slight, which we should not have expected, as it seemed probable that the introduction of the nitrous-acid radicle (ONO) would have increased the ease with which the hydrogen in the other malonic ester radicle was removed.

A solution of the sodium salt of the nitrite of trinitrophenylenedimalonic ester was made by adding one drop of sodic hydrate solution to a large excess of the ester moistened with alcohol, and, after the action had taken place, diluting with much water. The solution thus obtained was of the color of a solution of potassic dichromate, but much less strongly colored than the solutions of the salts of any of the related substances. Its action with the various reagents was tried, and the following characteristic precipitates observed:

With *barium salt*, rather heavy yellow flocks.

With *mercurous* or *lead salts*, heavy yellow flocks.

With *silver* or *copper salts*, yellow flocks.

Salts of *calcium*, *strontium* or *magnesium* gave only faint yellow precipitates, decidedly different from the heavy one produced by baric chloride.

Nitrite of Bromdinitrophenylmalonic Ester, $C_6H_2Br.(NO_2)_2.C.NO_2.(CO.OC_2H_5)_2$.

Although bromdinitrophenylmalonic ester does not change in color when heated with nitric acid, as has been stated more than once in previous papers[1] from this Laboratory, it really is affected in the same way as the corresponding trinitro-compound, being converted into its nitrite, but without the formation of the red secondary product which made the reaction so striking in that case. The substance was prepared as follows: A small quantity of the bromdinitrophenylmalonic ester (melting-point 75°–76°) was heated on the steam-bath with nitric acid of specific gravity 1.38 for five minutes, or longer (as the same compound was obtained if the heating was continued three hours). There was at first no sign of a reaction except a slight evolution of nitrous

[1] This Journal **11**, 99; **12**, 8.

fumes; but as the heating continued, the undissolved solid melted, forming an oil drop, which after cooling solidified to a mass of crystals, while at the same time the acid liquid deposited crystals looking very much like those of the bromtrinitrophenyltartronic ester. All of these crystals were purified by recrystallisation from boiling alcohol, until they showed the constant melting-point 111°, when they were dried at about 70° and analysed with the following results:

I. 0.1973 gram substance gave on combustion 0.2492 gram carbonic dioxide and 0.0510 gram H_2O.

II. 0.2084 gram substance gave 17.4 cc. nitrogen at a temperature of 22° and a pressure of 755.6 mm.

	Calculated for $C_6H_2Br.(NO_2)_2.C.NO_2.(CO_2C_2H_5)_2$.	Found. I.	II.
Carbon	34.66	34.44	...
Hydrogen	2.67	2.87	...
Nitrogen	9.33	...	9.41

The substance therefore is the nitrite of the bromdinitrophenylmalonic ester, and not the corresponding tartronic ester, as we had expected from the long heating used in one of the methods of preparation, and from the fact that no difficulty was encountered in making the combustion of it.

Properties.—The nitrite of bromdinitrophenylmalonic ester crystallises usually in thick rhombic crystals often one millimeter in each direction, which look somewhat like rhombohedra with a sharp acute angle, but are seen to be twins by the lines of twinning and striations; the obtuse angles on these crystals are often truncated. Less commonly with the characteristic forms just described, long flattened prisms occur, which are terminated by a single plane at a sharp acute angle, rarely by two. It is easy to see that the rhombic crystals could be formed by the twinning of these prisms. The crystals are very lustrous, of a white color, with a slight greenish cast, and melt at 111° without decomposition. The substance is essentially insoluble in cold water, very slightly soluble in hot; soluble in cold alcohol, more so, but still far from freely, in hot. It shows no signs of decomposition when boiled with alcohol. It is more soluble in methyl than in ethyl alcohol, cold or hot; very freely soluble in benzol, chloroform or acetone; freely soluble in glacial acetic acid; soluble in ether or carbonic disulphide; nearly, if not quite, insoluble in ligroine.

Hot alcohol is the best solvent for it. Strong sulphuric acid has no action on it in the cold, but when hot dissolves a little of the substance after it has melted; strong hydrochloric acid has no action, hot or cold; strong nitric acid has no action on it in the cold, but when hot dissolves a little of it, which is deposited on cooling. Neither acid sodic carbonate nor neutral potassic carbonate had any action with it, even in presence of alcohol; sodic hydrate in aqueous solution was without action; if alcohol was added, a portion of the substance dissolved slowly with a yellow color, but most of the white crystals were left unattacked; ammonic hydrate in aqueous solution had no action, with alcohol little or none. The substance behaves, therefore, as we should expect, a salt being formed only by a reagent like sodic hydrate strong enough to remove the nitro group attached to the side-chain.

The nitrite of bromdinitrophenylmalonic ester is much more stable than the corresponding trinitro-compound, since it is not decomposed by boiling with alcohol, or at its melting-point or by boiling with nitric acid; for, as has been already stated, it could be made by boiling for three hours with nitric acid, whereas under these conditions the trinitro-compound was converted into the tartronic ester. Nor did longer boiling of the dinitro-compound with nitric acid produce the tartronic ester, as even after seven hours it showed the melting-point of the unaltered substance 111°. As the trinitrotartronic ester had been obtained also by heating the corresponding nitrite, we tried the same experiment with the dinitronitrite, and found that, when heated a few degrees above its melting-point, it turned rather dark-colored and gave off bubbles of gas, in which bromine was recognised by the smell. The residue was oily, but after solution in alcohol crystals were obtained which showed the characteristic rhombic form of the nitrite of bromdinitrophenylmalonic ester. This experiment therefore seemed to show that the action of heat consisted only in the complete decomposition of a portion of the nitrite of bromdinitrophenylmalonic ester, and, as it did not promise to give the desired tartronic ester, further work in this direction was abandoned.

Reduction of the Nitrite of Bromdinitrophenylmalonic Ester.

The conversion of the nitrite of bromtrinitrophenylmalonic ester into the corresponding tartronic ester by nitric acid, or by the action of heat, indicates that the group NO_2 in the side-chain is

attached to the molecule by oxygen instead of nitrogen, or, in other words, that the substance is a nitrite, and not a nitro-compound; but, as we could not consider this a conclusive proof of the oxygen attachment, we have studied the reduction of a body of this class, selecting for this purpose the dinitro-compound, because it is more easily prepared than the corresponding substance containing three nitro groups, and also because the product obtained from it by reduction would probably be more stable than one containing one more amido group.

Six grams of the nitrite of bromdinitrophenylmalonic ester, divided into three lots of two grams each, were mixed with granulated tin, strong hydrochloric acid, and a few drops of alcohol, and after adding a piece of platinum to accelerate the reaction, were allowed to stand on a steam radiator (50°–70°) until all the organic matter had dissolved, and no further action was observed, which happened usually in about an hour and a half. If quantities larger than two grams were used a very dark colored solution was obtained. The solution poured off from the excess of tin was freed from stannous and stannic chlorides by means of sulphuretted hydrogen, when a residue was obtained by evaporation of the filtrate, which gave off ammonia gas when treated with an alkaline hydrate, and formed a precipitate of ammonic chlorplatinate with chlorplatinic acid; it evidently, therefore, contained ammonic chloride in addition to the chloride of the organic base. The washings of the sulphide of tin, which were worked up separately from the filtrate, on the other hand, yielded crystals which showed only a very slight amount of ammonic chloride by the same tests, and accordingly these crystals were dried at 100°, and analysed with the following results:

I. 0.1980 gram substance gave 25.25 cc. nitrogen at a temperature of 23° and a pressure of 764.8 mm.

II. 0.1954 gram substance gave by the method of Carius 0.1480 gram Ag Cl.

	Calculated for $C_6H_3.NH_2Cl(CH.OH.CO.NH)$.	Found. I.	Found. II.
Nitrogen	13.96	14.47	...
Chlorine	17.70	...	18.73

These results are not all that we could wish; but although they show the presence of the small amount of ammonic chloride, which we had detected by the qualitative tests, they leave no

doubt in regard to the composition of the organic substance, and therefore we have not thought it worth while to spend the great amount of time which would have been necessary to prepare a sample entirely free from ammonic chloride; especially as these analyses prove that the group NO_2 is attached to the side-chain by oxygen, since we obtained, by the reduction of the nitrite of bromdinitrophenylmalonic ester, ammonic chloride and the chloride of amidoxyoxindol instead of the chloride of diamidoxindol, which would have been formed if the group NO_2 had been attached to the molecule by the nitrogen.

Properties of the Chloride of the Amidoxyoxindol, $C_6H_3.NH_2Cl.(CH.OH.CO.NH)$.

This substance was obtained crystallised in rather large plates, usually in forms like a closed fan terminated by an obtuse angle, and set in rows one over the other with the obtuse angles parallel, or arranged in branching arborescent forms like coral; sometimes in thicker sharp prisms. It had a dark yellow color, as we observed it; was soluble in cold water, more so in hot; slightly soluble in cold or hot alcohol, and insoluble, or nearly so, in most of the other solvents. The strong acids gave no striking reactions with it, except strong nitric acid, which turned it orange-red; but this seemed to be due to some nitrous acid in the nitric, as on the addition of sodic nitrite the color was much intensified. Sodic hydrate added to the aqueous solution gave a few brown flocks, evidently from decomposition of a part of the base; ammonic hydrate gave a tolerably heavy, flocculent precipitate, at first whitish, but turning brown on exposure to the air, but it showed no signs of crystallisation, and with the small amount of substance at our disposal we have been unable to obtain the free base in any definite form. The chloride mixed with alcohol and some strong hydrochloric acid imparted after some time a dark red color to a piece of pine wood.

Attempt to make Dinitrophenylenedimalonic Ester.

The results just described having shown that the behavior of bromdinitrophenylmalonic ester toward nitric acid was not so different from that of the trinitro-compound as we had at first supposed, it became of interest to determine whether other apparent differences between these two bodies were no better

marked, and accordingly we tried to make the dinitrophenylenedimalonic ester by the method which had given good results with the trinitro-compound as follows: 3 grams of bromdinitrophenylmalonic ester were dissolved in ether, and, after the addition of 1.5 grams of malonic ester previously treated with 0.15 gram of sodium in a large quantity of alcohol, the mixture was boiled under a return-condenser for three hours; at the end of this time the solution had turned deep red, and a little solid had separated. The product was treated with water and dilute sulphuric acid, the ether separated, and the aqueous liquid tested for sodic bromide, which it was found to contain in small quantity, but the crystals deposited by the ether melted after one crystallisation at 75°–76°, the melting-point of bromdinitrophenylmalonic ester. We infer from this experiment, therefore, that, although a little dinitrophenylenedimalonic ester may have been formed, its quantity was exceedingly small, and that the reaction, if it goes on at all, certainly takes place with much more difficulty in the case of the dinitro- than in that of the trinitro-compound.

LXXIV.—NOTE ON TRIBROMMONONITROBENZOL.

By C. Loring Jackson and W. B. Bentley.

The results of experiments on the behavior of tribromtrinitrobenzol and tribromdinitrobenzol with various reagents have been described in a number of papers from this Laboratory. For the sake of completeness, we felt it necessary to include the tribrommononitrobenzol in our investigation, and were the more inclined to do this as we hoped that it might throw some light on the replacement of bromine by hydrogen, so often observed in our work with the trinitro- and dinitro-compounds. This hope has not, however, been fulfilled, as no such replacement of bromine by hydrogen was observed, and the tribrommononitrobenzol has proved to be so inert with various reagents that it deserves only the short investigation the results of which are given in this paper.

The tribrommononitrobenzol used in this work was prepared by boiling symmetrical tribrombenzol (melting-point 119°) for fifteen minutes with a nitric acid made by adding to fuming nitric acid (specific gravity 1.51) one-quarter of its volume of common strong nitric acid (specific gravity 1.38). The greater part of the

tribrommononitrobenzol separated as the mixture cooled, and the rest was obtained by the addition of water to the acid mother-liquor. This process gave better results than when acetic acid was used to dilute the fuming nitric acid according to the method given by V. von Richter.[1]

Action of Tribrommononitrobenzol with Sodic Ethylate.

The tribrommononitrobenzol melting at 125° was acted on by hot sodic ethylate, giving a substance which we found it convenient to prepare as follows: 5 grams of tribrommononitrobenzol dissolved in benzol were mixed with an alcoholic solution of the sodic ethylate from 1 gram of sodium, heated on the water-bath just below boiling for some time, and then allowed to stand at a temperature a little above the ordinary for several hours. The red solution thus obtained was filtered from a precipitate which had formed (this gave a test for bromide with argentic nitrate), diluted with water, and acidified with dilute sulphuric acid, after which the benzol was separated from the aqueous liquid: this was extracted with ether, and the combined extracts from the organic solvents purified by crystallisation from alcohol until the constant melting-point 91° was reached. Sometimes a black tarry product was obtained from the reaction, instead of the white crystals formed if the process had gone well. This tarry mass was worked up most conveniently by distillation with steam, followed by crystallisation of the steam distillate from alcohol. The pure substance was dried at about 70°, and analysed with the following results:

I. 0.1900 gram substance gave by the method of Carius 0.2181 gram AgBr.

II. 0.3800 gram substance gave 15.9 cc. nitrogen at a temperature of 22° and a pressure of 756.5 mm.

	Calculated for $C_6H_2Br_2.NO_2.OC_2H_5$.	Found. I.	Found. II.
Bromine	49.22	48.85	...
Nitrogen	4.31	...	4.72

The substance is therefore dibromnitrophenetol, and was formed by the replacement of one atom of bromine by the ethoxy radicle.

Properties.—The dibromnitrophenetol crystallises in bundles of prisms, which are usually somewhat flattened and terminated by a basal plane, also occasionally showing with this two other

[1] Ber. d. chem. Ges. **8**, 1426.

planes at an obtuse angle to each other. It is white, but turns brown on exposure to the air; melting-point 91°; essentially insoluble in cold water, perhaps very slightly soluble in hot; alcohol dissolves it sparingly when cold, freely when hot; more soluble in methyl than in ethyl alcohol; very freely soluble in benzol, chloroform, acetone, or carbonic disulphide; freely soluble in ether; slightly soluble in cold glacial acetic acid, soluble in hot; very slightly soluble in ligroine. The best solvent for it is hot alcohol. It distils with steam. Strong sulphuric acid has no action in the cold, but when hot gradually forms a black solution; cold nitric acid has no action on it, but when hot dissolves it, depositing crystals on cooling, which seem by their melting-point to be the unaltered substance; strong hydrochloric acid seems to have no action, whether hot or cold; sodic hydrate seems not to act upon it.

Action of other Reagents on Tribrommononitrobenzol.

Sodic methylate behaved in much the same way as the sodic ethylate, except that it was necessary in this case to heat for a longer time, and even after this a certain amount of tribrommononitrobenzol was apt to be left unaltered. The product after crystallisation from alcohol showed the constant melting-point 104°, but its analyses gave percentages of bromine differing from those corresponding to dibromnitroanisol by about 1 per cent. The cause of this is probably the same as that of the similar want of agreement between the calculated and observed percentages in the case of the bromdinitroresorcin dimethylether;[1] but we have not thought the substance of sufficient importance to try to obtain better analytical results, which, to judge by our work on the bromdinitroresorcin dimethylether, would be a matter of great difficulty.

From these experiments it appears that the tribrommononitrobenzol acts with sodic alcoholates less easily than the tribromdinitrobenzol, which is attacked by them in the cold, forming the ethers of bromdinitróresorcin, whereas it is necessary to heat the mononitro-compound to bring about any action. When the tribromdinitrobenzol is heated with an alcoholate, the third atom of bromine is replaced by hydrogen and an ether of the dinitroresorcin is formed, but we found no trace of any action of this sort with the mononitro compound. It is to be noted, too, that

[1] This Journal **13**, 175.

only one atom of bromine is removed from the mononitro-, but two from the dinitro-compound.

The inertness of tribrommononitrobenzol as compared with the corresponding dinitro-compound is made even more evident by the study of the action of aniline upon it. This substance converts tribromdinitrobenzol into trianilidodinitrobenzol, when heated with it for a short time, whereas the corresponding trinitro-compound is formed in the cold; from the mononitro-substance we were unable to obtain any anilido-compound, even after heating for some time to the boiling-point of aniline; a little aniline bromide was formed, it is true, but almost all of the tribrommononitrobenzol was recovered unaltered, as recognised by its melting-point and very characteristic crystalline form.

No better result was obtained with sodium malonic ester, which acts on the dinitro- and trinitro-compounds in the cold, but even after boiling for some time with the tribrommononitrobenzol yielded only a very small quantity of sodic bromide, while almost all of the tribrommononitrobenzol was recovered unaltered.

Contribution from the Laboratory of General Chemistry, University of Michigan.

ON THE SAPONIFICATION OF THE SUBSTITUTED ACETIC ESTERS.

By Paul C. Freer and F. L. Dunlap.

As the study of organic chemistry has progressed, the influence exerted by negative atoms or groups of atoms upon the compounds in which they enter as constituent parts, has frequently been the subject of remark. It is a well-known fact, for instance, that the introduction of acetyl or carbethoxyl in place of hydrogen in acetic ester renders the remaining hydrogen atoms so reactive that they can act as if they belonged to an acid substance, while a substitution of a nitro-group in methane or ethane can cause a similar change to take place in those bodies.

It seems, *a priori*, then, reasonable to assume that organic acids, like acetic acid, will suffer an increase in their avidity by the introduction of chlorine or bromine in place of hydrogen, and

furthermore, this avidity should be greater in the monochlor-acid than in the monobrom-acid, for chlorine is more negative in its nature than bromine, as can readily be seen from the relative stability of the hydrogen compounds of the two halogens, and the same relationship should exist between the dichlor- and dibrom- and the trichlor- and tribrom-acids. That this is the case is shown by the work of Ostwald,[1] who has proved the avidity of the three chlorine substituted acetic acids, as measured by their electric conductivity, to be as follows:

Acetic acid,	$K =$ 0.00189
Monochlor-acetic acid,	$K =$ 0.155
Dichlor-acetic acid,	$K =$ 5.17
Trichlor-acetic acid,	$K =$ 121.

From these investigations another fact becomes apparent, namely, that the introduction of the first chlorine atom exerts a greater influence than that of the second, while the further substitution of remaining hydrogen atom does not influence the avidity in nearly the same degree as the respective replacement of hydrogen by the other two; for the influence of each successive chlorine atom, beginning with acetic acid, is in the ratio of 86 : 33 : 24. Ostwald further found the constant for monobrom-acetic acid to be 0.138, a number somewhat less than that found with monochlor-acetic acid.

It occurred to us that a similar relationship as was observed by Ostwald in the avidity of the acids in question would be found in their rapidity of saponification; the ethyl ester of the acid displaying the highest constant as determined by Ostwald, should also be most readily saponified, while a successive diminution of this rate should be observed accompanying the elimination of each chlorine atom and its replacement by hydrogen. Some work on the velocity of saponification has been done by Ostwald,[2] who studied the hydrolysis of methyl acetate in presence of various free acids, finding the amount of change in the unit of time much increased by the acid addition. Ostwald studied incomplete reactions, determining the amount of free acid formed from time to time by titration with a standard baryta solution. R. B. Warder[3] also devoted some time to the study of the speed of saponification, using ethyl acetate and sodium hydroxide in dilute aqueous solu-

[1] Ztschr. phys. Chem. **3**, 176. [2] J. prakt. Chem. [2] **28**, 449.
[3] This Journal **3**, 340; Ber. d. chem. Ges. **14**, 1361.

tion. The latter investigator endeavored to discover the relationship between the temperature of a reaction and the velocity thereof, and came to the conclusion that the increase in the speed is approximately as the second power of the temperature, a relationship which agrees with that suspected by Hood[1] from a study of the action of potassium chlorate on ferrous sulphate. Reicher[2] has also undertaken a similar investigation, studying the influence of temperature on the velocity of saponification of acetic ester by means of a solution of sodium hydroxide. He, like Warder, does not complete the reaction, but titrates from time to time, in order to determine the amount of free alkali present.

Remsen and Hillyer[3] at a later date worked out a method for determining the relative stability of the alkyl bromides, and this was subsequently more fully carried out by Lengfeld.[4] The alkyl bromides, as well as the reagents used, were in alcoholic solution, and the decompositions were studied under the influence of sodium and potassium hydroxides, ammonia, silver nitrate, nitric acid, sulphuric acid and a mixture of silver nitrate and nitric acid. The substances to be decomposed were weighed in small bulbs and sealed. These were then placed in flask, the solution of the reagent added, the flask well stoppered and the bulbs broken. The amount of change was noted by opening sets of the bottles at stated intervals of time and titrating the amount of sodium bromide formed, and the work was carried out at different temperatures, the result showing that the influence of temperature varied with the reaction under consideration. We also arrived at this conclusion after having carried out the series of experiments with the substituted acetic esters, for, as a glance at the appended table will show, this influence is much more apparent in the case of the mono-substituted esters than it is with the di- and tri-substituted ones, and, despite the limited number of results which we are at this time able to present, it seems scarcely possible that the speed of the reactions is approximately as the second power of the temperatures.

The work on the saponification of the substituted esters has, up to the present, only been extended so as to include monochlor-, dichlor- and trichlor-, and monobrom-, dibrom- and tribrom-acetic acids, and has, so far as the relative influence of the halogen atoms upon the speed of the saponification is concerned, fully

[1] Phil. Mag. [5] **6**, 383.
[2] This Journal **8**, 151.
[3] Ann. Chem. (Liebig) **228**, 257; **232**, 103; **238**, 276.
[4] Ibid. **11**, 40.

answered our expectations, for, as will be seen from the plotted curves, the tri-substituted acids are more rapidly saponified than di-substituted ones, and the latter more rapidly than the mono-substituted, and furthermore it becomes apparent that bromine does not exert quite as marked an influence as chlorine. Our work differs from that which has previously been done in two particulars: we used molecular quantities of base and acid, and allowed complete saponification to take place. The results of this research agree with a statement made by Conrad and Brückner[1] that the rapidity of saponification of the esters of the acids of the fatty series increases with the strength of the acid.

Experimental Part.

In the course of this research we studied the saponification of monochlor-, dichlor- and trichlor-acetic esters, and of the corresponding bromine compounds. We endeavored to extend the investigation so as to include the iodo- and nitro-esters, but were compelled to abandon this purpose on account of the instability of the substances in question.

The apparatus used was a modification of that recommended by Beckmann[2] for the determination of molecular weights by the lowering of the freezing-point of solutions, the outer jar being filled with water, which, during any given saponification, was kept at a constant temperature.

The quantity of ester to be saponified was in each case so selected as to be exactly hydrolysed by 5 cc. of a solution of barium hydroxide saturated at 15° C.; 5 cc. of this solution were found to contain 0.22355 gram of barium. The calculated quantities of the various esters which were used in each operation are given below:

For ethyl monochlor-acetate, 0.2350 gram.
" ethyl dichlor-acetate, 0.3011 "
" ethyl trichlor-acetate, 0.3672 "
" ethyl monobrom-acetate, 0.3203 "
" ethyl dibrom-acetate, 0.4718 "
" ethyl tribrom-acetate, 0.6232 "

The amounts of the pure esters necessary for each saponification were respectively weighed into small glass bulbs and sealed for future use.

[1] Ztschr. phys. Chem. **7**, 290. [2] Ibid. **2**, 638.

All of the barium hydroxide solution used in the research was prepared at the same time and was placed in a large bottle fitted with a double-bored stopper and two bent glass tubes, one reaching to the bottom of the flask, the other to the bottom of the stopper. The glass tube which extended into the solution was attached to one of the vents of a double-stopcock burette, while the one terminating at the bottom of the stopper was connected with a wash-bottle containing caustic potash solution; the entrance of carbon dioxide to the top of the burette was prevented by connecting with a tower filled with soda-lime. The bottle containing the baryta solution was placed upon a rack several feet above the level of the table upon which the operations were to be conducted, so that by this means the burette could be emptied and filled at pleasure without allowing any acids which might be present in the atmosphere to come in contact with the standard solution, the value of which was unaltered during the entire research. The apparatus just described is a modification of that devised by Knöfler.

The method for conducting any given saponification was as follows:

Into a large glass test-tube, which extended down into the outer jar of the Beckmann apparatus which was filled with water, one of the small glass bulbs containing a weighed amount of ester was dropped, and 75 cc. of a diluent composed of equal parts of water and alcohol were then added, care being taken to have the diluent exactly at the temperature of the bath. After adding a few drops of phenol phthalein to the contents of the test-tube, the bulb was broken by a glass rod and the mixture agitated until homogeneous; 5 cc. of baryta were then run in, and the interval of time necessary for the disappearance of the color of the indicator noted; the solution in the meanwhile being constantly agitated by means of the glass rod, while the temperature of the bath, which during any saponification was kept constant, was noted. This process was repeated at temperatures ranging from 0° to 60°, the experiments not being carried beyond the latter point, for at about 60° the alcohol begins to be volatilised in such quantities as to affect the volume of diluent. The alcohol used in this work was absolutely free from acid. In the experiments conducted at 0° we, of course, experienced no difficulty in maintaining a constant temperature by means of melting ice, and the bath was brought to the other

points by mixing together waters of differing temperatures until the desired one was obtained, and afterward but little trouble was experienced in preventing a variation.

Saponification of Ethyl Monochlor-acetate.

Monochlor-acetic ester was prepared by means of alcohol and dry hydrochloric acid. The substance used had a constant boiling-point from 141° to 142°, and upon analysis gave the following figures:

0.2358 gram ester gave 0.2752 gram AgCl.

	Calculated.	Found.
Cl	28.95	28.86

The results of the saponification were as follows:

Amount of ester, 0.2350 gram; amount of $Ba(OH)_2$ solution, 5 cc.

Experiment.	Time (Minutes).	Temperature.
1	84	0°
2	55	8
3	39	14.5
4	27	23
5	17.5	32
6	11	41
7	9	47
8	6	60

Ethyl Dichlor-acetate.

This was prepared in a manner similar to that used for the ethyl monochlor-acetate. The ester has a boiling-point of 156°–157°. An analysis resulted as follows:

0.4011 gram of the ester gave 0.7311 AgCl.

	Calculated.	Found.
Cl	45.19	45.18

Upon saponification, the ester gave the following figures:

Amount of ester, 0.3011 gram; amount of $Ba(OH)_2$ solution, 5 cc.

Experiment.	Time (Minutes).	Temperature.
1	9.5	0°
2	8.5	8
3	7.5	15
4	5.75	27
5	3.5	37
6	2.5	46.5
7	1.25	56

Ethyl Trichlor-acetate.

This substance was prepared in the same way as the ethyl monochlor- and dichlor-acetates; it is a colorless liquid with an odor resembling that of oil of wintergreen; its vapors but slightly attack the eyes; its boiling-point is 164°.

0.2173 gram of the ester gave 0.4874 AgCl.

	Calculated.	Found.
Cl	55.58	55.49

The saponification gave the following figures:

Amount of ester, 0.3672 gram; amount of $Ba(OH)_2$ solution, 5 cc.

Experiment.	Time (Minutes).	Temperature.
1	7.5	0°
2	5.25	12
3	4.75	15
4	3.25	26
5	1.25	39
6	.5	49
7	.25	55

Ethyl Monobrom-acetate.

The same method was used here as was used in the formation of the preceding esters; however, the addition of hydrochloric acid gas to the alcoholic solution of monobrom-acetic acid causes a slight separation of bromine. For purification, the ester was distilled under diminished pressure, boiling at 73°–75° (40 mm.).

0.1937 gram ester gave 0.2178 AgBr.

	Calculated.	Found.
Br	47.87	47.84

The following results were obtained upon saponification:

Amount of ester, 0.3203 gram; amount of $Ba(OH)_2$ solution, 5 cc.

Experiment.	Time (Minutes).	Temperature.
1	90	0°
2	67	8
3	50	15
4	36	24
5	22	36
6	15	43
7	10	52
8	7	60

Ethyl Dibrom-acetate.

This ester was prepared according to the method of Remi[1] by heating bromal with potassium cyanide and alcohol.

Some difficulty was experienced in obtaining a sufficient yield of bromal by following Löwig's method,[2] so that we finally decided upon the following modification, which has shown itself to be entirely satisfactory:

To 150 cc. absolute alcohol, in a flask fitted with an inverted condenser, 135 cc. anhydrous bromine are slowly added by means of a dropping-funnel. After the addition of the bromine, the liquid is boiled upon a water-bath until hydrobromic acid ceases to pass off, when, upon cooling, the liquid separates into two layers. The whole is then placed in a large flask and treated with concentrated sulphuric acid until the violent action accompanied by an evolution of hydrobromic acid has ceased, when a layer of dark-red liquid forms at the bottom of the flask. This portion is separated from the one above and fractioned, the fraction between 165°–180° containing the bromal; and from this, bromal hydrate will separate upon the addition of a small quantity of water and cooling. The hydrate must be kept in the dark in a closed bottle, otherwise slight decomposition sets in.

In order to prepare ethyl dibrom-acetate, the bromal hydrate was treated according to Remi's method,[3] with the difference that after allowing the mixture of bromal hydrate and a saturated alcoholic solution of potassium cyanide to stand for about twenty-four hours, we then finally boiled for some time in a flask fitted with an inverted condenser. Upon fractioning the decanted liquid, the portion boiling between 185°–193° contains the desired ester. To purify this, it was fractioned under diminished pressure, boiling between 101°–102°, 6 mm.

0.2301 gram of the ester gave 0.3513 AgBr.

	Calculated.	Found.
Br	65.01	64.96

The saponification of this ester gave the following figures:

Amount of ester, 0.4718 gram; amount of $Ba(OH)_2$ solution, 5 cc.

[1] Ber. d. chem. Ges. **8**, 695. [2] Ann. Chem. (Liebig) **3**, 288.
[3] Ber. d. chem. Ges. **8**, 695.

Experiment.	Time (Minutes).	Temperature.
1	19.5	0°
2	14.0	9
3	10	17
4	7	29
5	5	38
6	3	48
7	2	60

Ethyl Tribrom-acetate.

To the chemically pure tribrom-acetic acid an excess of absolute alcohol was added, and this solution was then saturated with pure, dry hydrochloric acid gas. This whole was then shaken out with water and the precipitated ester separated as nearly as possible from the supernatant liquid and first dried over calcium chloride, and then, after filtering, was finally allowed to stand for several days in a sulphuric-acid desiccator. The ester thus prepared is always slightly colored by bromine; the latter was removed by means of molecular silver. It was found impossible to fraction this ester even *in vacuo*, as considerable decomposition always takes place,—a portion distilling at 139° (38 mm.) upon analysis gave only 80 per cent. of the calculated bromine,—so that we were compelled to use the undistilled product in our work.

The following analysis shows, however, that this was nearly pure:

0.2211 gram of the ester gave 0.3828 AgBr.

	Calculated.	Found.
Br	73.82	73.67

The saponification gave the following results:

Amount of substance, 0.6232 gram; amount of $Ba(OH)_2$ solution, 5 cc.

Experiment.	Time (Minutes).	Temperature.
1	17	0°
2	12	10
3	8.5	17
4	6.5	26
5	3.5	38
6	2.0	47
7	1.5	53
8	1.0	60

Finally, ethyl monochlor-acetate was also saponified with 25 cc. diluent to see what influence, if any, the quantity of the latter might have on the reaction.

The results of this saponification, which are given in the following table, show that the figures differ but little from those obtained with a 75-cc. solution.

Experiment.	Time (Minutes).	Temperature.
1	80	0°
2	53	8
3	36	15.5
4	24	24.5
5	16	33
6	10	41
7	7.5	52.5
8	5.5	59

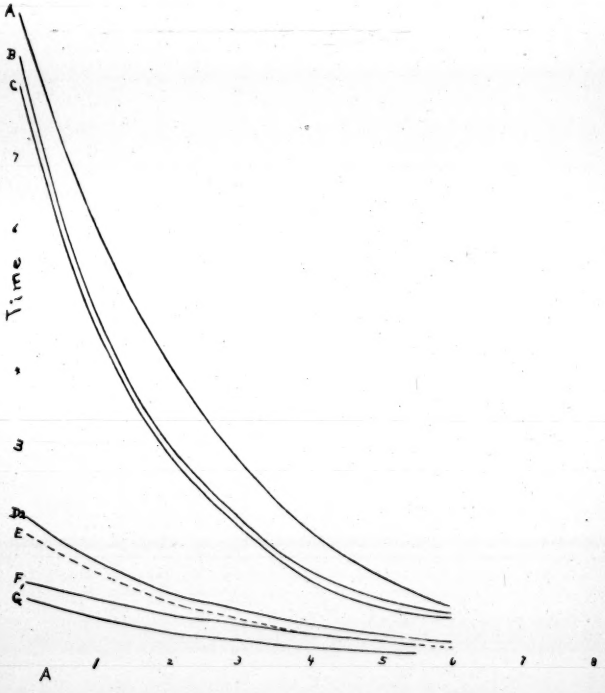
A glance at the above results will show that, although the relationship between the times of saponification at any given temperature are not similar to that obtaining between the avidities as developed by Ostwald, yet the acids maintain the same relative positions, namely, those with the greatest avidities are most readily saponified. This can be readily seen by a comparison of the results at 0°:

Monochlor-acetic ester, time, 84 minutes,
Dichlor-acetic ester, time, 9.5 minutes,
Trichlor-acetic ester, time, 7.5 minutes,
Monobrom-acetic ester, time, 90 minutes,
Dibrom-acetic ester, time, 19.5 minutes,
Tribrom-acetic ester, time, 17 minutes.

Another result also becomes apparent, namely, that the introduction of the second chlorine or bromine atom exerts a much greater influence than that of the third. Whether the exact influence exerted by a substituting halogen atom in any compound of the fatty series can, in the future, be calculated by a mathematical formula will only become apparent after an extended investigation of these compounds, although one result can already be predicted, namely, that the influence of the halogen atoms on the rate of saponification will diminish according to their distance from the carbethoxyl group. The discovery that an increase in temperature has a greater relative effect on the speed of saponifi-

cation of the mono-substituted acids than it has on the di-substituted ones is not unexpected, when we consider that any such acceleration is due to an increase in the molecular motion, and hence to an increasing number of impacts between the base and ether in the unit of time; as a consequence, those molecules with the smallest mass will have their velocity of motion advanced in a greater degree for an equal change in temperature than will those with the larger.

The results of these determinations have been plotted as curves upon the following table, the time of reaction being taken as ordinates and the temperatures as abscissæ:



Contribution from the Chemical Laboratory of the University of Illinois.

I.—A NOTE UPON THE REDUCTION OF SYMMETRICAL TRIAMIDO-TRINITRO-BENZENE.

By Arthur W. Palmer.

In a paper by C. L. Jackson and J. F. Wing upon tribrom-trinitro-benzene published nearly five years ago,[1] the authors record the results of a preliminary attempt to obtain hexamido-benzene, $C_6(NH_2)_6$, by reduction of the symmetrical triamido-trinitro-benzene, $C_6(NH_2)_3(NO_2)_3$, and express the intention of continuing the work, a promise referred to later in a paper upon pentamido-benzene by Jackson and Palmer.[2] At the invitation of Professor Jackson I undertook the study of the reaction, and, although the desired end has not been attained, yet the results seem to be of sufficient interest to warrant a publication of them. The symmetrical triamido-trinitro-benzene used was prepared by the method described by Jackson and Wing,[3] from tribrom-trinitro-benzene prepared according to the directions given in the same article. The tribrom-trinitro-benzene so obtained melted sharply at 285° (uncorrected). By treatment in the cold with alcoholic ammonia for twenty-four hours, then boiling with reverse-cooler for a half-hour, more alcoholic ammonia being added from time to time, the conversion into triamido-trinitro-benzene was completed.

The product, filtered off, was washed with alcohol, then with water and, finally, boiled out several times with chloroform. This product was not analysed, as it in every way corresponded with the product obtained in this same way by Jackson and Wing and analysed by them. The first attempts at reduction were carried out by use of tin and hydrochloric acid, but, as had before been found by Jackson and Wing, the results were unsatisfactory, and it was thought best to try zinc dust and glacial acetic acid, because it was hoped that an acetyl compound would be formed which might be expected to be more stable than the chloride or other salt and consequently more easily handled. It was found, however, that no such acetyl compound was obtained, the product consisting mostly of ammonium chloride (in one case with an

[1] Proc. Am. Acad. **23**, 142; This Journal **10**, 283.
[2] Proc. Am. Acad. **24**, 105; This Journal **11**, 448.
[3] Loc. cit.

unmanageable black tar which may have proceeded from the decomposition of the hexamido-benzene), and this was the result although the mixture was kept cool during the reduction, protected from air, and evaporated, after removal of the zinc, at a pressure of 5 to 7 mm. As these results were so unpromising, the method by treatment with tin and hydrochloric acid was again resorted to. At first an attempt was made to purify the product of the reduction by the method of Nietzki with sulphuric acid and alcohol, but with no favorable result. I accordingly proceeded as follows:

2.06 grams symmetrical triamido-trinitro-benzene, $C_6(NH_2)_3(NO_2)_3$, 15 cc. of alcohol, 25 cc. of hydrochloric acid and the quantity of tin required by theory (8.48 grams) were placed in a flask together. The reaction proceeded slowly, but all of the tin disappeared before the reduction was complete, so 2 grams more tin were added, and after a few days the solution became colorless, and a considerable quantity of white crystalline substance remained in place of the original dark-orange substance. The crystalline substance was filtered off, washed with alcohol, in which it is slightly soluble, then several times with ether, and dried. As it was found to contain tin, it was dissolved in water, the tin removed by sulphureted hydrogen and the filtrate saturated with hydrochloric acid gas. The crystals formed in this way were filtered off and dried. The substance crystallised in long, colorless, acicular prisms which darken gradually when exposed to the air. The aqueous solution quickly turns blue, then, after some time, black, and a black amorphous precipitate separates. An analysis of the crystals led to the identification of the substance as the hydrochloride of pentamido-benzene.

I. 0.1779 gram substance, slightly, but only superficially darkened, gave 0.1859 gram CO_2 and 0.0895 gram H_2O.

II. 0.1453 gram substance gave 33.8 cc. of moist nitrogen gas at 11.8° C. and 745 mm. pressure.

III. 0.1474 gram substance, treated by Carius' method, gave 0.2377 gram AgCl.

	Calculated for $C_6H(NH_2)_5(HCl)_2$.	Found. I.	II.	III.
Carbon	27.43	28.49	...	...
Hydrogen	5.33	5.59	...	...
Nitrogen	26.67	...	27.08	...
Chlorine	40.58	...	...	39.78

As it now seemed that the difficulties met with had been the result of over-reduction, new attempts were made, the only modification of the method being the use of less than the theoretically required quantity of tin. 3.5 grams of pure triamido-trinitro-benzene were mixed with 30 cc. of alcohol and 40 cc. of fuming hydrochloric acid, and 5 grams of tin added: the reaction started at once, and five days later 5 grams more tin were added and the mixture saturated with hydrochloric acid gas.

$$C_6(NH_2)_3(NO_2)_3 + 9Sn + 18HCl = C_6(NH_2)_6 + 6H_2O + 9SnCl_2.$$

By a study of the course of the reaction it was found from direct tests that the chief product of the reaction is $SnCl_2$ and that only very small quantities of $SnCl_4$ are at any time formed:

$$2C_6(NH_2)_3(NO_2)_3 + 9Sn + 36HCl = 2C_6(NH_2)_6 + 12H_2O + 9SnCl_4.$$

According to the equation, the quantity of tin required by theory for reduction of 3.5 grams of triamido-trinitro-benzene is 14.38 grams. When the tin had entirely disappeared, the liquid, although deeply colored and containing much of the triamido-trinitro-benzene still unchanged, was saturated with hydrochloric acid gas and the precipitate filtered off and washed with fuming hydrochloric acid and then with alcohol. The residue, on a Gooch filter, was extracted with water, which left the triamido-trinitro-benzene undissolved—the filtered solution treated with sulphureted hydrogen until all the tin was precipitated, and the solution, now free of tin, saturated with hydrochloric acid gas. The crystals which separated gave all of the reactions of pentamido-benzene hydrochloride, and some of the product was analysed with the following results:

I. 0.2016 gram substance yielded 0.2032 gram CO_2 and 0.1044 gram H_2O.

II. 0.1350 gram substance gave 34.4 cc. of moist nitrogen gas at 22° C. and 744 mm. pressure.

	Calculated for $C_6H(NH_2)_5(HCl)_3$.	Found. I.	Found. II.
Carbon	27.43	27.49	...
Hydrogen	5.33	5.75	...
Nitrogen	26.67	...	27.51
Chlorine	40.58	...	...

Another reduction, run in the same way, but by use of 15 grams of tin to 5.75 grams of triamido-trinitro-benzene, resulted simi-

larly, but the product was not analysed. Theory requires for 5.75 grams of triamido-trinitro-benzene 23.69 grams of tin.

The results herein noted appear to establish the fact that upon reduction of triamido-trinitro-benzene, $C_6(NH_2)_3(NO_2)_3$, at least one amido group or one nitro group is replaced by hydrogen—a result similar to that already noticed by Nietzki[1] and Hagenbach in their attempt to obtain pentamido-benzene by reduction of their mononitro-derivative of diethenyl-tetramido-benzene.

ON THE FORMATION OF LAYERS IN SOLUTIONS OF SALTS IN MIXTURES OF WATER AND ORGANIC LIQUIDS.

By C. E. Linebarger.

It has been known for a very long time that if potash be added to weak alcohol, two well-defined layers will separate out, the upper one consisting of a little of the salt, dissolved in a mixture of little water and much alcohol, and the lower one of the greater part of the salt dissolved in a mixture of much water and little alcohol. This has been turned to practical account in the concentration of alcohol. Raymond Lully (A. D. 1235) seems to be the first chemist, or rather alchemist, who makes mention of the phenomenon, but it was probably known long before his time, as little originality is to be found in his writings.

We find no record of the phenomenon with other salts than potash, or other liquids than alcohol, up to the year 1830, when Brandes,[2] in the course of an investigation on the hydrates of manganous sulphate, observed that under certain conditions of temperature and concentration in a solution of manganous sulphate in a mixture of alcohol and water, a layer like a heavy oil collects at the bottom of the vessel. Brandes merely makes passing mention of the fact and does not concern himself about its explanation. Some thirty years afterwards Hugo Schiff[3] rediscovered the fact.

[1] Ber. d. chem. Ges. **20**, 331, 2114. [2] Ann. der Phys. Pogg. **20**, 586.
[3] Ann. Chem. (Liebig) **118**, 362.

In determining the solubility of certain salts in mixtures of alcohol and water of varying strengths, he found that a 15 to 50 per cent. spirit, when saturated with manganous sulphate, separated into two layers, the lower one containing much salt and little alcohol, the upper one much alcohol and little salt. This separation does not take place at the ordinary temperature, when an alcohol of less than 15 or more than 50 per cent. is taken.

At a higher temperature, however, layers form even with an alcohol of 13 per cent. or one of 60 per cent. and between. Experiments showed that if 100 volumes of solvent be saturated with manganous sulphate, the upper layer occupied:

When 20 per cent. spirits was used, 16 volumes.
" 30 " " " " " 44 "
" 40 " " " " " 66 "

Percentage of alcohol, ...	20	30	40
Percentage weight of salt dissolved, upper layer,	2.2	1.66	1.31
Percentage weight of salt dissolved, lower layer,	47	48	48.6

And the upper layers contain from 50 to 55 per cent. alcohol; the lower, 12 to 14 per cent.

The above is essentially all that Schiff did on the subject, and matters rested so until 1887, when J. Traube and O. Neuberg[1] took up the subject, and found that many other salts had this peculiarity of causing their solution in alcohol and water to separate into layers. They examined more closely the layers formed in a system consisting of ammonium sulphate, alcohol and water, in order to see if the layers were formed in molecular proportions. Although their experimental data are insufficient to permit the drawing of any general conclusions, yet they established the following facts, viz., as the temperature increases—

1) in the upper layer, there is a decrease in the amount of salt and water and an increase in the amount of alcohol;

2) in the lower layer, the amount of water increases and the amount of salt and alcohol decreases.

As the change in the composition of the lower layer is, however, so insignificant, even when the temperature changes considerably, they think that the composition of the lower layer may be regarded as approximately constant.

They found further that, as the amount of salt or alcohol increases (even at different temperatures) there is—

[1] Ztschr. phys. Chem. **1**, 509.

1) in the upper layer a decrease in the amount of water and salt and an increase in the amount of alcohol;

2) in the lower layer, a decrease in the amount of alcohol and an increase in the amount of salt, while the amount of water first increases, then decreases.

The question whether or not the layers have a composition according to molecular proportions could not be answered decisively.

Pharmacists[1] have observed that, in filling certain prescriptions, a separation into layers takes place. For instance, if chloral be added to a solution of potassium bromide in weak spirits, layers separate out. Likewise layers are formed when potassium acetate is added to the fluid extract of buchu. In this connection may be mentioned the observation made by Parmentier[2] that certain complex inorganic acids are soluble in ether only within certain limits, an excess of the solvent causing a separation into layers. I have found also that many organic substances have this property of forming layers. Thus cane-sugar in aqueous solution forms layers with alcohol and with acetone; glycerine in alcoholic solution forms layers if ether and benzene be added; and such instances might be greatly multiplied.

Here, then, is a class of phenomena of solutions of which but relatively little is known. All investigations on the subject have been carried out with but few salts and ethyl alcohol. J. Traube and C. Neuberg having found[3] that methyl alcohol does not, and isoamyl alcohol does bring about the formation of layers in an aqueous solution of ammonium sulphate, say that perhaps similar phenomena might be observed in other organic series. The conditions of layer-formation seem to be two freely miscible liquids and a substance quite soluble in one and insoluble in the other. But one cannot say that any substances that fulfill these conditions will form layers. Heretofore the liquids have been ethyl alcohol and water; the substances, manganous sulphate (Schiff), ammonium sulphate (Traube and Neuberg) and potassium carbonate. I have taken up the subject with the intention of finding out what substances are capable of forming these layers, what the limits of layer-formation are, and what the composition of the layers may

[1] Private communication by Prof. Miner of Illinois College of Pharmacy.
[2] Compt. rend. **104**, 686.
[3] Ztschr. phys. Chem. **1**, 514.

be. I have limited myself thus far to four organic liquids—methyl alcohol, ethyl alcohol, propyl alcohol, and acetone—all of which are freely soluble in water, and to about seventy typical salts. I will divide the subject into three parts: 1. The examination of the behavior of the salts towards mixtures of water and the above organic liquids as regards the formation of layers. This part is essentially qualitative. 2. The determination of the limits of the formation of layers under varying conditions of temperature and concentration. 3. The determination of the composition of the two layers together with their specific gravities and surface tensions.

Part I.

The experiments were carried out as follows: To a saturated solution of a salt contained in a test-tube the organic liquid was added little by little, with vigorous agitation, until either a layer formed or the salt was precipitated. In the cases where no layer formed, the liquid added would sometimes readily mix with the water, forming a quite good solvent for the salt, so that it was necessary to add a relatively large amount to bring about precipitation, and sometimes the first drops added would cause a precipitate to form. It is necessary to work with very concentrated solutions and to add the organic liquid slowly, since some of the salts form layers only within narrow bounds, which cannot be detected except by operating carefully. All the experiments were repeated with a solution of the salt half as concentrated, entirely similar results, with one or two exceptions, being obtained.

The results of the experiments are given in the following table, in which the first column gives the name of the salt and the second its chemical formula.

Table.[1]

Name of Salt.	Formula.	$CH_3.OH$.	$C_2H_5.OH$.	$C_3H_7.OH$.	$(CH_3)_2CO$.
Lithium chloride,	LiCl	*n*	*n*	*n*	*y!*
Ammonium "	NH_4Cl	*n*	*n*	*y*	*y!*
Sodium "	NaCl	*n*	*n*	*y!*	*y!*
Potassium "	KCl	*n*	*n*	*y!*	*y!*

[1] *y* = forms layers with water and the organic liquid at the head of the column.
n = forms no layers as above given.
y! = layers are formed within wide limits.
y_n = layers are formed only within narrow limits.
n_e = forms no layers; salt is quite soluble in a mixture of water and organic liquid.
n_p = forms no layers; salt is quite insoluble in a mixture of water and organic liquid.

Name of Salt.	Formula.	$CH_3.OH.$	$C_2H_5.OH.$	$C_3H_7.OH.$	$(CH_3)_2CO.$
Rubidium chloride,	$RbCl$	n_e	n_e	$y\,!$	$y\,!$
Calcium "	$CaCl_2$	n_e	n_e	y	$y\,!$
Strontium "	$SrCl_2$	n_e	n_e	n_e	y
Barium "	$BaCl_2$	n_e	n_e	n_e	n
Nickel "	$NiCl_2$	n_e	n_e	n_e	n_e
Cobalt "	$CoCl_2$	n_e	n_e	n_e	y_w
Copper "	$CuCl_2$	n_e	n_e	n_e	y_w
Cerium "	$CeCl_4$	n_e	n_e	n_e	n_e
Aluminium "	Al_2Cl_6	n	n	n	n
Ferric "	Fe_2Cl_6	n_e	n_e	n_e	n_e
Manganese "	$MnCl_2$	n_e	n_e	n_e	$y\,!$
Cadmium "	$CdCl_2$	n_e	n_e	n_e	n_e
Zinc "	$ZnCl_2$	n_p	n_p	n_p	n_p
Mercuric "	$HgCl_2$	n_e	n_e	n_e	n_e
Magnesium "	$MgCl_2$	n_e	n_e	n_e	n_e
Stannous "	$SnCl_2$	n	n	n	n
Ammonium acetate,	$NH_4(C_2H_3O_2)$	n_e	n_e	n_e	n_e
Sodium "	$NaC_2H_3O_2$	n_e	n_e	n_e	n_e
Potassium "	$KC_2H_3O_2$	n_e	n_e	n_e	$y\,!$
Nickel "	$Ni(C_2H_3O_2)_2$	n_e	n_e	n_e	n_e
Manganese "	$Mn(C_2H_3O_2)_2$	n_e	n_e	n_e	y
Magnesium "	$Mg(C_2H_3O_2)_2$	n_e	n_e	n_e	n_e
Lead "	$Pb(C_2H_3O_2)_2$	n_e	n_e	n_e	n_e
Ammonium nitrate,	NH_4NO_3	n_e	n_e	n	n
Sodium "	$NaNO_3$	n_e	n_e	$y\,!$	n_e
Potassium "	KNO_3	n_p	n_p	n_p	n_p
Calcium "	$Ca(NO_3)_2$	n_e	n_e	n_e	n_e
Strontium "	$Sr(NO_3)_2$	n_e	n_e	y	n_e
Barium "	$Ba(NO_3)_2$	n_p	n_p	n_p	n_p
Magnesium "	$Mg(NO_3)_2$	n_e	n_e	n_e	n_e
Nickel "	$Ni(NO_3)_2$	n_e	n_e	n_e	n_e
Cobalt "	$Co(NO_3)_2$	n_e	n_e	n_e	n_e
Mercurous "	$Hg(NO_3)$	n_e	n	n_p	n_p
Lead "	$Pb(NO_3)_2$	n_p	n_p	n	n_p
Lithium sulphate,	Li_2SO_4	n_p	n_p	$y\,!$	$y\,!$
Sodium "	Na_2SO_4	n_p	y	$y\,!$	y
Potassium "	K_2SO_4	n	n	n	n
Ammonium "	$(NH_4)_2SO_4$	n	y	y	y

Name of Salt.	Formula.	$CH_3.OH$.	$C_2H_5.OH$.	$C_3H_7.OH$.	$(CH_3)_2CO$.
Nickel sulphate,	$NiSO_4$	n_p	n_p	y	$y!$
Cobalt "	$CoSO_4$	n_p	n_p	y_w	y
Copper "	$CuSO_4$	n_p	n	$y!$	n_p
Ferrous "	$FeSO_4$	n	n?	$y!$	n_p
Ferric "	$Fe_2(SO_4)_3$	n_e	n_e	y_w	y_w
Cadmium "	$CdSO_4$	n_e	y_w	y	y
Zinc "	$ZnSO_4$	n	y	y	y
Chromium "	$Cr_2(SO_4)_3$	n_e	n_e	n	n
Manganese "	$MnSO_4$	n	$y!$	$y!$	$y!$
Ammonium hydrate,	NH_4OH	n_e	n_e	n_e	n_e
Sodium "	$NaOH$	n	y_w	$y!$	$y!$
Potassium "	KOH	n	y_w	$y!$	$y!$
Barium "	$Ba(OH)_2$	n	n_p	n_p	n_p
Ammonium carbonate,	$(NH_4)_2CO_3$	n_e	n	n_p	n_p
Sodium "	Na_2CO_3	n	$y!$	$y!$	$y!$
Potassium "	K_2CO_3	y_w	$y!$	$y!$	$y!$
Lithium "	Li_2CO_3	n_p	n_p	n_p	n_p
Sodium bicarbonate,	$NaHCO_3$	n_p	n_p	n_p	n_p
Cadmium iodide,	CdI_2	n_e	n_e	n_e	n_e
Potassium "	KI	n_e	n_e	n_e	n_e
Sodium "	NaI	n_e	n_e	n_e	n_e
Ammonium bromide	NH_4Br	n_e	n_e	n_e	n_e
Sodium "	$NaBr$	n_e	n_e	n_e	n_e
Potassium "	KBr	n_p	n_p	n_p	n_p
Potassium cyanide,	KCN	n_e	n_e	$y!$	$y!$
Potassium ferricyanide,	K_3FeCy_6	n_p	n_p	y_w	n_p
Potassium ferrocyanide,	K_4FeCy_6	n_p	n_p	n_p	n_p
Magnesium bromide,	$MgBr_2$	n_e	n_e	n_e	n_e

The table shows certain regularities in regard to the formation of layers. The chlorides generally do not exhibit this phenomenon. The group of the chlorides of the alkaline metals are, however, a notable exception. All of these form layers in a mixture of acetone and water, and, save lithium, in a mixture of propyl alcohol and water. It is seen also that the higher the molecular mass, the wider are the limits of layer-formation; and the table shows that lithium chloride with the smallest molecular mass does not form layers in propyl alcohol, while ammonium chloride

possessing the next smallest molecular mass does so within quite narrow limits. It would seem, then, that there is an intimate relation between the molecular masses and the capability of causing a separation into two layers in solutions; in the case of the alkaline chlorides, the smaller the molecular mass, the less pronounced this peculiarity of layer-formation. The chlorides of the alkaline earths, on the other hand, behave in exactly the opposite way. Here the smaller the molecular mass, the more readily does the formation of layers take place. Thus, calcium chloride (molecular mass = 111) forms layers in mixtures both of propyl alcohol and water and of acetone and water; strontium chloride (molecular mass 158.5) only in mixtures of acetone and water, while barium chloride (molecular mass = 208) forms no layers at all. There is, therefore, a regular gradation according to the molecular masses of the chlorides. It is noteworthy that manganese chloride forms well-defined layers with acetone and water.

With but few exceptions, the acetates and nitrates do not cause a separation into layers. It is worth while to note that the salts sodium nitrate and strontium nitrate, that form layers in mixtures of propyl alcohol and water by exception, contain as base those elements which are the second members in the triads: lithium, *sodium*, potassium; calcium, *strontium*, barium.

But the sulphates and carbonates exhibit this peculiarity of layer-formation in the most marked degree. Thus sodium and potassium carbonates form layers within wide limits with ethyl and propyl alcohols and acetone. Potassium carbonate, however, is the only salt forming layers with methyl alcohol, and that, too, within narrow limits.

The alkali sulphates—with the exception of potassium sulphate, which owes its behavior to its slight solubility—form layers in mixtures of propyl alcohol and water and of acetone and water, as well as in mixtures of ethyl alcohol and water. To this last statement lithium sulphate, however, forms an exception. The rest of the sulphates examined all form layers, except chromium sulphate, with propyl alcohol and water, and copper, ferrous and chromium sulphate, with acetone and water. Only with zinc, manganese and cadmium sulphates are layers with ethyl alcohol and water obtained.

Sodium and potassium hydrates form layers in mixtures of the three organic liquids, respectively, with water.

Taking now the organic liquids into consideration, we see that only methyl alcohol forms layers with potassium carbonate. Ethyl alcohol and water together with several salts form layers, while propyl alcohol and water, and acetone and water form layers with a still greater number of salts. It is seen that without exception any salt that forms layers in a mixture of ethyl alcohol and water, does so also in mixtures of propyl alcohol and water, and acetone and water, and the layers are generally formed within wider limits. In the case of the alcohols, then, the greater the molecular mass, the more pronounced the formation of layers. Propyl alcohol and acetone which have almost equal atomic masses do not, however, behave in the same way as regards the formation of layers. Thus in the case of the chlorides and acetates, acetone sometimes causes the formation of layers, where propyl alcohol does not, while in the case of the nitrates just the opposite takes place. The property of forming layers seems to depend upon the nature of the acid part of the salt and not upon its base.

Part II.

The formation of layers in a system consisting of a salt, an organic liquid and water takes place only within certain limits. This second part of the investigation gives these limits for certain salts which possess in a marked degree the peculiarity of forming layers in mixtures of (1) ethyl alcohol and water, (2) propyl alcohol and water, (3) acetone and water.

Determination of the "Upper" Limit of Layer-formation.

By "upper" limit is meant the limit attained when the formation of a layer is rendered impossible by the presence of too much organic liquid. Experimentally it was difficult to determine this limit with any degree of accuracy. As the alcohol or acetone, as the case may be, becomes more concentrated, the salt becomes more insoluble and generally separates out before the limit is reached. Although I tried several salts, it was only with potassium carbonate that I was able to obtain trustworthy data. With the other salts, crystallisation always took place long before the true limit was attained, so that layers and solid salt were present at the same time.

The determinations were carried out as follows: A certain

volume of a titrated solution of salt was introduced into a graduated tube such as is used in gas analysis, and small quantities of organic liquid added from time to time. After the addition of each portion of alcohol or acetone, the contents of the tube were vigorously agitated and the tube placed in a vertical position in a place where the temperature varied but little. After a couple of hours the volumes of the layers were read off and alcohol again added. This was continued until no layer remained at the bottom of the tube. As stated above, all the salts with the exception of carbonate of potassium were precipitated before the layer disappeared. In the case of this latter salt, crystals appeared as soon as the layer disappeared.

I give the results of a determination carried out with potassium carbonate, ethyl alcohol and water.

4 cc. of solution were taken containing 0.592 gram K_2CO_3 and 3.8 grams H_2O.

Successive additions of alcohol,	6 cc.	6	4	4	6	8	12	10	5	5	4
Total alcohol added,	6 cc.	12	16	20	26	34	46	56	61	66	70
Volume of upper layer,	8.6 cc.	15.6	18.6	23.	29.8	36.9	49.2	59.7	62.	66.4	70.6
Volume of lower layer,	1.1 cc.	1	0.9	0.8	0.6	0.5	0.	30.2	0.1	0.1	0

As 70 cc. of the alcohol used contain 1.75 grams water and 54.5 grams absolute alcohol, the upper limit is reached in a system consisting of 54.5 grams alcohol, 5.5 grams water, and 0.592 gram potassium carbonate.

Two other determinations, made by adding at once nearly enough alcohol to cause the disappearance of the lower layer, and then approaching by small quantities the requisite amount, gave:

I. 54.1 grams alcohol; 5.5 grams water; 0.592 gram carbonate.

II. 53.8 grams alcohol; 5.3 grams water; 0.592 gram carbonate.

Considering the difficulties of the determinations, the agreement can be regarded as entirely satisfactory.

Determination of the "Lower" Limit of Layer-formation.

By "lower" limit is understood the point where a layer ceases to form, on account of the presence of an excess of water. The determinations of this limit can be made with great accuracy. If

water be added slowly to a solution separated into layers, at the point where it is impossible to distinguish them as such the solution turns milky; also when a layer commences to form, this same milkiness is apparent. But a single drop of water is necessary, when the limit is reached, to cause the solution to become perfectly clear. The determinations were accordingly made as follows: Varying quantities of organic liquid and water were added from burettes to a titrated solution of a salt until a drop of water would clear up the milkiness caused by a drop of alcohol. So sharply defined is this point that a single drop of alcohol caused a distinct cloudiness in a clear solution of potassium carbonate just ready to separate into layers.

The details of the operation are the following: A known volume of a titrated salt solution was run into a bottle fitted with a good glass stopper. A little organic liquid was then run in from a burette and enough water added to render the solution clear. The bottle was then placed in a thermostat, and when its contents had acquired the desired temperature, enough of the organic liquid was added to cause a cloudiness to appear. The bottle was then replaced in the thermostat. If its contents again became clear a little more organic liquid was added. This was repeated until a *drop* of water would clear up the milkiness occasioned by a drop or so of alcohol. The burettes were then read off and the process repeated by adding more organic liquid and water. After a little experience the determinations can be made very accurately and quickly.

When comparatively large quantities of organic liquid and water had been added, the point where the solution turned milky was not so easy to discern. But as, before this point was reached, enough determinations could be made to show the behavior of the solution, that circumstance has but little weight.

As temperature had no little influence upon the formation of layers, before giving the results of my determinations I will describe some experiments made with the intention of finding out just what this influence was.

Influence of Temperature upon the Formation of Layers.

In general, it may be stated that the lower the temperature the more water is needed to bring about the disappearance of the layers. A fall of a few degrees of temperature will bring about

the characteristic cloudiness in a solution of potassium carbonate in a mixture of alcohol and water just on the point of forming layers, and this cloudiness will disappear on warming to the previous temperature. The experiments were carried out with potassium carbonate, ethyl alcohol and water.

I placed in each of four glass-stoppered bottles 10 cc. of solution containing 1.48 grams K_2CO_3 and 9.5 grams water, and then added (1) to first bottle 20 cc. alcohol (= 15.6 grams C_2H_6O and 0.5 gram H_2O); (2) to second bottle 30 cc. alcohol (= 23.4 grams C_2H_6O and 0.75 gram H_2O); (3) to third bottle 40 cc. alcohol (= 31.2 grams C_2H_6O and 1 gram H_2O); (4) to fourth bottle 50 cc. alcohol (= 39 grams C_2H_6O and 1.25 grams H_2O).

The bottles were heated in a thermostat to 55.5° C. and water added until the cloudiness just disappeared. It was found necessary to add to

	(1)	(2)	(3)	(4)
Water in cc.	6.8	11.3	15.7	18.9

The temperature was then allowed to fall to 19.4° C., when, to cause the ensuing cloudiness to disappear, I had to add to

	(1)	(2)	(3)	(4)
Water in cc.	1	1.4	1.9	3.2

I prepared another similar set of bottles, heated them to 44° C., and added, to just cause turbidity, to

	(1)	(2)	(3)	(4)
Alcohol in cc.	1.1	1.7	2.1	2.5

On raising the temperature to 61.6° it was necessary to add to

	(1)	(2)	(3)	(4)
Alcohol in cc.	0.5	0.7	0.9	1.1

The results of the experiments are regular and entirely concordant among themselves. They show how great is the influence of temperature, and that it is necessary, in order to obtain strictly comparable results, to take it into account. In all the determinations I made the temperature of the solutions was 20° C.

The results of the determinations of the lower limits of the formation of layers are given in the following tables. These need no special explanation, with the exception perhaps of the last two columns. Here "water × const." and "alcohol × const." indicates that the water and alcohol are multiplied by a number which is the reciprocal of the weight of the salt. The quantities

of alcohol and water are thus referred to unit weight of salt, which renders all the tables comparable.

The salts used were all by individual tests found to be strictly chemically pure. A concentrated solution was made of each, and the salt therein determined gravimetrically. By taking the specific gravity of the solution, the amount of water present was easily determined. The methyl alcohol was from the establishment of Kahlbaum and labeled "*puriss. acetonfrei.*" Its specific gravity at 18° was 0.7953. The ethyl alcohol was prepared by distilling ordinary spirits over quicklime. Its specific gravity at 15° was 0.8002, and, therefore, contained two per cent. of water by weight; a correction is made for this water in the tables. The propyl alcohol was chemically pure, with a specific gravity of 0.8075 at 15°. The acetone was chemically pure and had a specific gravity of 0.796 at 15°.

I.—*Potassium carbonate; methyl alcohol; water.*

2 cc. of solution containing 1 gram K_2CO_3 and 1.63 grams H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol in grams.
I	0.64	2.27	3.2	2.54
II	0.87	2.5	4.1	3.26
III	1.6	3.23	8.5	6.76

II.—*Potassium carbonate; ethyl alcohol; water.*

1 cc. of solution containing 0.148 gram K_2CO_3 and 0.95 gram H_2O.

	Water in cc.	Water in Alcohol.	Total Water.	Alcohol in cc.	Absolute Alcohol in grams.	Water ×7.	Alcohol ×7.
I	2.15	0.15	3.25	5.	3.85	22.7	26.9
II	3.72	0.29	4.96	10.1	7.77	34.7	53.3
III	5.1	0.45	6.5	15.5	11.95	45.5	83.6
IV	6.4	0.6	7.95	20.	15.4	55.6	107.8
V	7.6	0.78	9.33	25.	19.22	65.3	134.5
VI	8.7	0.9	10.55	30.	23.1	73.8	161.7

III.—*Potassium carbonate; propyl alcohol; water.*

1 cc. of solution containing 0.148 gram K_2CO_3 and 0.95 gram H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water ×7.	Alcohol ×7.
I	0.95	1.90	1.6	1.28	13.3	8.9
II	4.1	5.05	7.9	6.34	35.3	44.3
III	5.5	6.45	11.9	9.54	45.1	66.7
IV	5.8	6.75	12.6	10.	47.2	70.
V	9.3	10.25	24.5	19.6	71.7	137.2

IV.—*Potassium carbonate; acetone; water.*

1 cc. of solution containing 0.5 gram K_2CO_3 and 0.88 gram H_2O.

	Water in cc.	Total Water.	Acetone in cc.	Acetone in grams.	Water × 2.	Acetone × 2.
I	3.72	4.60	3.	2.4	9.2	4.8
II	7.2	8.08	7.4	5.92	16.1	11.4
III	10.2	11.08	11.8	9.44	22.1	18.8
IV	14.65	15.53	19.3	15.44	31.1	30.8
V	18.4	19.28	26.9	21.52	38.5	43.

V.—*Potassium carbonate; acetone; water.*

2 cc. of solution containing 0.296 gram K_2CO_3 and 1.9 grams H_2O.

	Water in cc.	Total Water.	Acetone in cc.	Acetone in grams.	Water × 3.4.	Acetone × 3.4.
I	1.12	3.02	2.	1.6	10.2	5.4
II	3.65	5.55	5.3	4.24	18.8	14.4
III	6.55	8.45	10.4	8.32	28.7	28.2
IV	9.5	11.4	18.4	14.72	38.7	50.0
V	12.8	14.7	33.	26.4	49.9	89.7

VI.—*Sodium carbonate; ethyl alcohol; water.*[1]

1 cc. of solution containing 0.293 gram Na_2CO_3 and 0.98 gram H_2O.

	Water in cc.	Water in Alcohol.	Total Water.	Alcohol in cc.	Absolute Alcohol in grams.	Water × 3.4.	Alcohol × 3.4.
I	7.7	0.27	8.95	9	6.93	30.4	23.6
II	9.8	0.34	11.12	11.6	8.94	37.8	30.4
III	13.4	0.58	14.96	19	14.62	50.86	49.7
IV	15.2	0.79	16.97	25.5	19.61	57.7	66.7

VII.—*Sodium carbonate; propyl alcohol; water.*

1 cc. of solution containing 0.293 gram Na_2CO_3 and 0.98 gram H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 3.4.	Alcohol × 3.4.
I	3.85	4.84	2.4	1.94	16.4	6.5
II	7.2	8.18	7.3	5.91	27.8	20.0
III	9.	9.98	10.6	8.59	33.9	29.2
IV	13.8	14.78	20.7	16.76	50.2	56.9
V	15.95	16.93	25.8	20.89	57.5	71.0
VI	18.7	19.68	33.	26.73	66.9	90.7

[1] Near the point of layer-formation, crystals separated out; that is, sodium carbonate is not very soluble in alcohol and water mixed in about the proportions necessary to produce layers. Hence the determinations in the above table are only approximately correct. They were made by adding alcohol rapidly to the solution containing an excess of water, and reading off without waiting long, so as to avoid the error due to the formation of the solid salt.

VIII.—*Sodium carbonate; propyl alcohol; water.*

0.5 cc. of solution containing 0.4165 gram Na_2CO_3 and 0.49 gram H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 6.8.	Alcohol × 6.8.
I	5.	5.49	5.7	4.62	37.4	30.4
II	10.2	10.69	18.5	14.98	72.7	102.
III	12.7	13.19	25.5	20.65	89.7	140.7

IX.—*Sodium carbonate; acetone; water.*

1 cc. of solution containing 0.293 gram Na_2CO_3 and 0.98 gram H_2O.

	Water in cc.	Total Water.	Acetone in cc.	Acetone in grams.	Water × 3.4.	Acetone × 3.4.
I	4.85	5.83	3.4	2.73	19.8	9.2
II	7.5	8.48	6.2	4.96	28.8	16.8
III	10.75	11.73	10.2	8.16	39.8	27.7
IV	13.7	14.68	14.15	11.32	49.9	38.4
V	16.4	17.38	18.9	15.12	59.1	51.3
VI	18.9	19.88	23.2	18.56	67.5	63.1
VII	21.	21.98	27.5	22.00	74.8	74.8

X.—*Sodium carbonate; acetone; water.*

0.5 cc. of solution containing 0.1465 gram Na_2CO_3 and 0.49 gram H_2O.

	Water in cc.	Total Water.	Acetone in cc.	Acetone in grams.	Water × 6.8.	Acetone × 6.8.
I	3.9	4.39	3.1	2.48	28.85	16.8
II	7.9	8.39	8.	6.4	57.55	43.5
III	8.4	8.89	8.6	6.88	60.4	46.9
IV	11.1	11.59	13.	10.4	78.8	70.7
V	15.	15.49	20.7	16.56	105.4	98.

XI.—*Ammonium sulphate; ethyl alcohol; water.*

1 cc. of solution containing 0.4084 gram $(NH_4)_2SO_4$ and 0.8 gram H_2O.

	Water in cc.	Water in Alcohol.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 2.5.	Alcohol × 2.5.
I	0.7	0.02	1.52	0.8	0.62	3.8	1.5
II	1.75	0.07	2.62	2.2	1.7	6.5	4.3
III	2.6	0.1	3.5	3.5	2.7	8.7	6.8
IV	3.95	0.18	4.93	6.25	4.82	12.3	12.1
V	6.56	0.37	7.73	12.8	9.87	19.3	24.7
VI	8.4	0.54	9.74	17.3	13.3	24.3	33.3
VII	15.4	1.22	17.42	40.8	31.42	43.4	78.5

XII.—*Ammonium sulphate; propyl alcohol; water.*

1 cc. of solution containing 0.4084 gram $(NH_4)_2SO_4$ and 0.8 gram H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 2.5.	Alcohol × 2.5.
I	3.3	4.1	1.4	1.12	10.7	2.8
II	6.8	7.6	7.5	6.0	19.0	15.0
III	8.4	9.2	11.	8.8	23.0	22.0
IV	12.1	12.9	20.8	16.64	32.2	41.6
V	15.3	16.1	30.9	24.72	40.2	61.8
VI	16.6	17.4	35.7	28.56	43.5	71.4

XIII.—*Ammonium sulphate; acetone; water.*

1 cc. of solution containing 0.4084 gram $(NH_4)_2SO_4$ and 0.8 gram H_2O.

	Water in cc.	Total Water.	Acetone in cc.	Acetone in grams.	Water × 2.5.	Alcohol ×2.5.
I	1.75	2.5	1.2	.96	6.4	2.4
II	5.	5.8	5.	4.	14.5	10.0
III	8.9	9.7	10.6	8.48	24.2	21.2
IV	13.2	14.	19.5	15.6	35.0	39.0
V	17.4	18.2	29.	23.2	45.5	58.0

XIV.—*Sodium sulphate; propyl alcohol; water.*

1 cc. of solution containing 0.1622 gram Na_2SO_4 and 0.98 gram H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol. in grams	Water × 6.2.	Alcohol × 6.2.
I	3.65	4.63	4.2	3.36	28.5	20.8
II	6.2	7.18	9.1	7.28	44.5	44.1
III	8.9	9.88	15.5	12.4	61.2	76.8
IV	11.7	12.68	20.65	16.52	78.6	102.4
V	13.3	14.28	27.3	22.04	88.5	136.6
VI	16.45	17.43	36.8	29.44	108.1	182.5

XV.—*Manganous sulphate; ethyl alcohol; water.*

1 cc. of solution containing 0.3205 gram $MnSO_4$ and 0.97 gram H_2O.

[1] Although layers formed in mixtures of sodium sulphate, ethyl alcohol and water, as well as of sodium sulphate, acetone and water, within not very narrow bounds, it was impossible to determine these limits with any degree of accuracy, since before the cloudiness indicative of the beginning of the separation of layers set in, salt crystallised out; I am unable, therefore, to give any data. With propyl alcohol and water, however, sodium sulphate formed very well defined layers.

	Water in cc.	Water in Alcohol.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 3.1.	Alcohol × 3.1.
I	1.	0.04	2.01	1.3	1.	6.2	3.1
II	4.9	0.19	6.06	6.4	4.93	18.7	15.3
III	6.8	0.29	8.06	9.9	7.63	24.9	23.7
IV	11.4	0.61	12.98	19.5	15.	40.2	46.5
V	15.	0.83	16.8	28.5	22.	52.	68.2

XVI.—*Manganous sulphate; propyl alcohol; water.*

1 cc. of solution containing 0.3205 gram $MnSO_4$ and 0.97 gram H_2O.

	Water in cc.	Total Water.	Alcohol in cc.	Alcohol in grams.	Water × 3.1.	Alcohol × 3.1.
I	3.2	4.17	2.3	1.84	12.9	6.8
II	6.8	7.77	6.8	5.44	24.0	16.8
III[1]	12.8	13.77	12.8	10.24	36.7	42.7
IV	14.2	15.17	18.2	14.56	47.0	55.1

XVII.—*Manganous sulphate; acetone; water.*

1 cc. of solution containing 0.3205 gram $MnSO_4$ and 0.97 gram H_2O.

	Water in cc.	Total Water.	Acetone in cc.	Acetone in grams.	Water × 3.1.	Acetone × 3.1.
I	2.5	3.47	1.7	1.36	10.7	4.1
II	7.55	8.52	6.	4.8	26.4	14.8
III	12.	12.97	10.9	8.72	39.2	27.0
IV	16.2	17.17	15.8	12.64	53.2	38.1
V	22.	22.97	23.6	18.88	71.2	58.5
VI	25.1	26.07	28.	22.4	80.8	69.4
VII	31.	31.97	37.5	30.00	99.1	93.0
VIII	34.5	35.47	43.1	34.48	109.9	106.8

The results of the determinations are given graphically in Figs. I, II and III. The amount of organic liquid is measured along the axis of abscissæ, the amount of water along the axis of ordinates. The numbers are taken from the last two columns in the tables, so that the curves represent the number of parts by weight

[1] Here a curious phenomenon presented itself. On agitating the mixture of the two layers, no turbidity ensued, but a perfectly clear solution was obtained with no trace of layers. On letting it stand for a few minutes, however, well-defined layers separated out. Hence it was difficult to detect the beginning of the disappearance of the layers. By operating as follows I was withal able to determine the point with a fair degree of accuracy. After the addition of alcohol or water, as the case might be, the bottle was allowed to stand quietly in the thermostat for an hour or so. The least trace of a layer could then be detected by tipping the bottle on its side, when the layer would appear as a streak running along the side of the bottle.

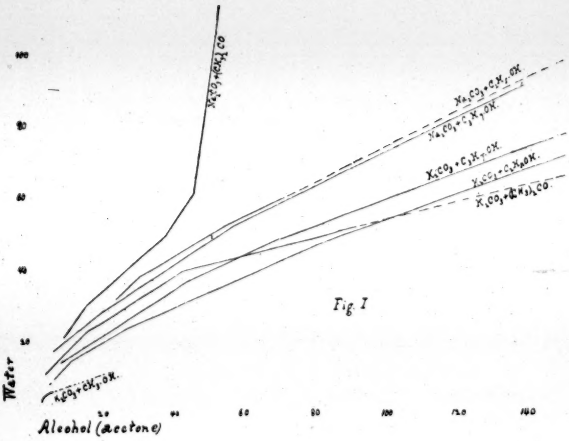


Fig. I

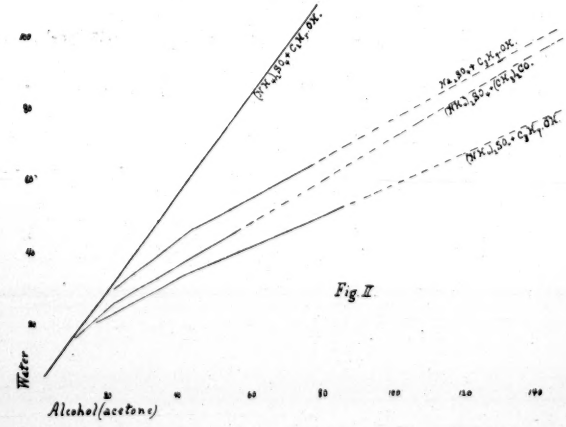


Fig II

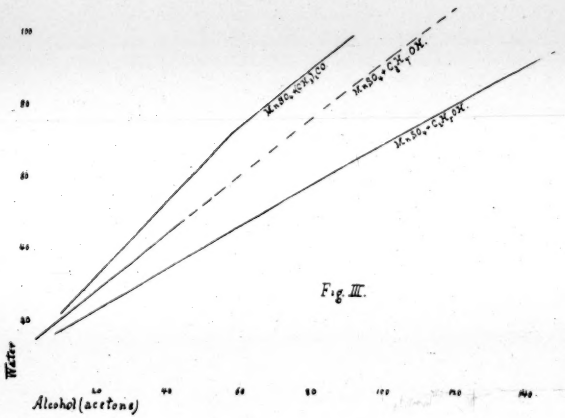


Fig. III.

of alcohol (acetone) and water present to one part of salt. The dotted portions of the curves are those which could not be determined experimentally, and are made by the continuation of the line passing through the last two points obtained. The curves have generally the same outline. They rise rapidly at first, and then gradually become more and more flattened. This means that when the amount of salt in the system is large in proportion to the quantities of organic liquid and water, the amount of water is relatively much greater than when the quantity of salt is small in proportion to the liquid constituents of the system. As the solution of the salt in the dissolving mixture becomes more dilute, the solution of the organic liquid in the water becomes more concentrated. The greater the mass of the solvent compared with the mass of the salt, the more organic liquid is present. The curves of the alkaline carbonates (Fig. I), as might be expected, are quite similar, with the exceptions of those where acetone is present. Potassium carbonate–ethyl alcohol–water and potassium carbonate–propyl alcohol–water, as well as sodium carbonate–ethyl alcohol–water, and sodium carbonate–propyl alcohol–water are quite parallel through their whole length, the curves of the sodium salt being situated higher up than those of the potassium salt.

The curves of sodium and ammonium sulphate (Fig. II) are quite similar. Sodium sulphate–propyl alcohol–water and ammonium sulphate–acetone–water lie quite close together, while ammonium sulphate–ethyl alcohol–water and ammonium sulphate–propyl alcohol–water are seen to diverge considerably. The curves for manganous sulphate (Fig. III) lie quite close together, and, as the tables show, the layers of the salt are formed within wide limits.

There is one curious fact to note concerning the curves in which propyl alcohol is found. The curve sodium sulphate–propyl alcohol–water lies almost exactly between the curves manganous sulphate–propyl alcohol–water and ammonium sulphate–propyl alcohol–water, and the molecular mass of sodium sulphate is just about the half of the sum of the molecular masses of the other two salts.

In Fig. I is given the curve for potassium carbonate–methyl alcohol–water. In comparison with the other systems in the figure, it is very short indeed. As stated in Part I, the greater the molecular mass of the alcohol in a system, the wider apart are, in general, the limits of layer-formation. Other analogies in the curves present themselves which will be more thoroughly discussed in Part III. The relations are very complicated, and it will be only by a thorough study of the composition of the layers and their physical constants that light may be obtained on the subject. I have already made numbers of determinations of the compositions of systems such as potassium carbonate–ethyl alcohol–water, sodium carbonate–ethyl alcohol–water and manganous sulphate–ethyl alcohol–water, and am waiting only until I shall have found a ready means for the analyses of propyl alcohol and acetone, to extend my investigations. I am led to believe that the study of the surface tensions will also throw some light upon the matter.

The third part of this research, together with some discussions and conclusions, I hope to have ready for publication in a few months.

CHICAGO, ILL.

REVIEWS AND REPORTS.

The Configuration of Grape-Sugar and its Isomers.

The researches of Emil Fischer upon the constitution and synthesis of sugars are well known through his numerous papers in the *Berichte*. The same have been reviewed in this Journal [1] and also in *Agricultural Science*.[2] These researches have now proceeded so far, and the results harmonise so entirely with the theory of the asymmetric carbon atom, that Fischer proposes, in two late papers,[3] to assign certain specific configurations to those of the sugars which have been well studied.

Bold as this undertaking seems, his conclusions, all based on experimental data, conform to the requirements of the theory and are ingeniously and skilfully drawn.

According to the theory there may exist sixteen isomers of the structure of grape-sugar, and for those derivatives of the same which have symmetrical molecules, *i. e.* dibasic acids and hexavalent alcohols, ten different structures are possible. These structures are expressed by the following table taken from van't Hoff-Herrmann's paper, "Die Lagerung der Atome im Raume," in which the signs + or — are used to indicate the relative arrangement of the hydrogen and hydroxyl upon the four non-terminal carbon atoms of the sugar molecule, accordingly as their sequence conforms to the direction in which the hands of a watch move, or the reverse.

				11	12	13	14	15	16
				+	+	+	+	+	—
				+	+	+	—	—	+
				+	—	—	+	—	—
				—	+	—	—	—	—
+	+	—	—	—	+	—	—	—	—
+	—	+	—	+	—	—	+	—	—
+	—	+	—	+	+	+	—	—	+
+	+	—	—	+	+	+	—	+	—
1	2	3	4	5	6	7	8	9	10

Of these it is evident that the arrangements 5–10 are identical with 11–16, so far as the alcohols or dibasic acids are concerned.

In order now to assign one of these configurations to grape-sugar upon the ground of experimental data it is necessary to con-

[1] **11**, 277 and **12**, 357. [2] **6**, No. 4. [3] Ber. d. chem. Ges. **24**, 1836 and 2683.

sider the saccharic acid of which both optical forms are known. The d. saccharic acid is derived from both the d. and l. glucose,[1] they being stereoisomeric. Hence the two acids must be included in cases 5–10, since only such can be derived from stereoisomeric sugars. But of these numbers, 7 and 8 are optically inactive and therefore not to be considered. Of the remaining cases, numbers 6 and 10 may also be rejected on the ground of the following experimental proofs.

Glucose and mannose differ from each other only in the configuration of the carbon atom, designated by an asterisk in the following formula,

$$CH_2OH.CHOH.CHOH.CHOH.{}^{*}CHOH.COH,$$

and the same, of course, holds true for their derivatives (sorbite and mannite, gluconic and mannonic acids, and saccharic and manno-saccharic acids). The proofs of this hypothesis are strong as presented by Fischer:

1. Mannose and glucose yield the same "osazon."[2]

2. Arabinose, by the addition of hydrocyanic acid, HCN, yields in the same reaction l. mannonic and l. gluconic acids.[3]

3. Fructose is reduced by sodium amalgam to a mixture of mannite and sorbite.[4]

4. Mannonic and gluconic acids, on being heated with pyridine or quinoline, are each transformed into the other.[5]

5. All attempts to separate mannonic or gluconic acids into different components have failed.[6]

Accepting these proofs of the relative structure of the above bodies, numbers 6 and 10 become impossible, for the following reasons: If saccharic acid, or what is the same thing, sorbite, had the structure 6, $+\ -\ +\ +$,

or 10, $-\ -\ +\ -$,

then the manno-saccharic acid or the mannite would have the structures 7, $-\ -\ +\ +$,

or 8, $-\ +\ -\ +$,

but these are both inactive combinations, while the mannite and manno-saccharic acid are both active.

There remain, therefore, for the d. and l. saccharic acids only the two configurations 5 and 9, and since it is immaterial just which arrangement of hydrogen and hydroxyl one understands by $+$ and which by $-$, Fischer assigns arbitrarily the configuration 5 to d. saccharic acid,

$$\begin{array}{l} COOH.CHOH.CHOH.CHOH.CHOH.COOH, \\ \qquad\quad -\qquad\quad +\qquad\quad +\qquad\quad + \end{array}$$

[1] Ber. d. chem. Ges. **24**, 521. [2] **22**, 374. [3] **23**, 2611. [4] **23**, 3684. [5] **23**, 800. [6] **23**, 800.

and 9 to the l. saccharic acid,

$$\begin{array}{c} \text{COOH.CHOH.CHOH.CHOH.CHOH.COOH.} \\ + \quad - \quad - \quad - \end{array}$$

But corresponding to the d. saccharic acid are two aldehyde sugars, d. glucose, or grape-sugar, and the d. gulose, a synthetic product. These, being stereoisomeric, would have the configurations,

$$\begin{array}{c} \text{5. COH.CHOH.CHOH.CHOH.CHOH.CH}_2\text{OH} \\ - \quad + \quad + \quad + \end{array}$$

and

$$\begin{array}{c} \text{11. COH.CHOH.CHOH.CHOH.CHOH.CH}_2\text{OH.} \\ + \quad + \quad + \quad - \end{array}$$

In order to assign one of these definitely to grape-sugar and the other to d. gulose it is necessary to again extend our observations to another series of sugars, viz. the pentoses.

From one of these, arabinose, is derived l. glucose, and from the other,[10] xylose, comes l. gulose. For these latter (l. glucose and l. gulose) there remain the configurations 9 and 15,

$$\begin{array}{c} \text{COH.*CHOH.CHOH.CHOH.CHOH.CH}_2\text{OH} \\ - \quad - \quad - \quad + \end{array}$$

and

$$\begin{array}{c} \text{COH.*CHOH.CHOH.CHOH.CHOH.CH}_2\text{OH.} \\ + \quad - \quad - \quad - \end{array}$$

In these formulas the asymmetric carbon atoms designated by the asterisk have been created by synthesis and do not exist in arabinose and xylose. Rejecting them, we have as the possible configurations of the two pentoses,

$$\begin{array}{c} \text{COH.CHOH.CHOH.CHOH.CH}_2\text{OH} \\ - \quad - \quad - \end{array}$$

and

$$\begin{array}{c} \text{COH.CHOH.CHOH.CHOH.CH}_2\text{OH.} \\ - \quad - \quad + \end{array}$$

For the pentoses of the structure of arabinose and xylose (aldehydes) there are eight possible isomers, or for the corresponding dibasic acids or alcohols the number is four, of which two are active and two inactive systems. The theoretical configurations of the two active forms of the dibasic acids are as follows:

$$\begin{array}{c} \text{COOH.CHOH.CHOH.CHOH.COOH} \\ + \quad + \quad + \\ \text{COOH.CHOH.CHOH.CHOH.COOH,} \\ - \quad - \quad - \end{array}$$

and of the inactive forms:

$$\begin{array}{c} \text{COOH.CHOH.CHOH.CHOH.COOH} \\ + \quad + \quad - \\ \text{COOH.CHOH.CHOH.CHOH.COOH.} \\ + \quad - \quad - \end{array}$$

[10] Ber. d. chem. Ges. **24**, 529.

The optical behavior of the acids or alcohols derived from arabinose and xylose would therefore serve to indicate in which of the above couples their configuration belongs. Here again the experimental testimony is clear, for both the arabite (upon the addition of borax) and the trioxy-glutaric acid from arabinose showed laevo-rotation. Arabinose, therefore, belongs to one of the two active systems, preferably the second, and its configuration would be as follows:

$$\underset{}{\text{COH.CHOH.CHOH.CHOH.CH}_2\text{OH.}}$$
$$\quad\;\; - \quad\;\; - \quad\;\; -$$

The xylose on the other hand belongs to the inactive systems, since the xylite, even with borax, and the trioxy-glutaric acid from xylose, are both without influence upon polarised light. To the xylose therefore is assigned this configuration:

$$\underset{}{\text{COH.CHOH.CHOH.CHOH.CH}_2\text{OH.}}$$
$$\quad\;\; - \quad\;\; - \quad\;\; +$$

The configurations thus experimentally indicated for these sugars would of course hold for their derivatives among the hexoses, viz. the l. glucose and l. gulose, and from these the configurations of other members of the group are easily deduced, as follows:

Hexose Sugars.

Aldoses.	COH.CHOH.CHOH.CHOH.CHOH.CH$_2$OH			
d. glucose,	−	+	+	+
l. glucose,	+	−	−	−
d. gulose,	+	+	+	−
l. gulose,	−	−	−	+
d. mannose,	+	+	+	+
l. mannose,	−	−	−	−

(For galactose the experimental data do not yet justify a choice between the four possible configurations indicated by a study of the mucic and allomucic acids.)

Ketoses.	COH.CO.CHOH.CHOH.CHOH.CH$_2$OH.		
d. fructose,	+	+	+
l. fructose,	−	−	−

The mono- and di-basic acids and hexavalent alcohols derived from these sugars retain their respective configurations, and we have therefore reasonable experimental proof of the configuration of upwards of twenty bodies which are either sugars or closely related to them.

Fischer takes good care to remark, however, that these conclusions can only stand provided the theory of the asymmetric carbon atom is wholly in accord with the facts, and provided the oxidation of arabinose and xylose to the respective trioxy-glutaric acids occurs without intramolecular changes.

In the expressions used above, however, the signs + and — may easily be misinterpreted, and to prevent confusion, Fischer in a second paper presents these configurations in a clearer manner. Taking the familiar models of the carbon atoms and constructing the sugar molecules according to the configurations proposed above, he develops graphic formulæ which have a new significance and permit an easy comparison of the different sugar molecules.

The four asymmetric carbon atoms may be designated by numbers as follows:

$$CH_2OH.\overset{1}{C}HOH.\overset{2}{C}HOH.\overset{3}{C}HOH.\overset{4}{C}HOH.COH.$$

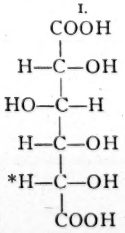
In the discussion of van't Hoff, upon which Fischer's deductions are based, the carbon atom 1 is compared only with 4, and 2 with 3. Consequently, in the configuration assigned to d. glucose or grape-sugar,

$$CH_2OH.\overset{1}{C}HOH.\overset{2}{C}HOH.\overset{3}{C}HOH.\overset{4}{C}HOH.COH,$$
$$\qquad\quad +\qquad\quad +\qquad\quad +\qquad\quad -$$

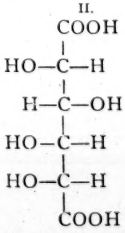
the arrangement of hydrogen and hydroxyl upon 1 is the opposite of that upon 4, while 2 and 3 are alike. If 1 be compared with 3 it is found that the arrangement is also the same. From a superficial examination the same would seem to follow for 1 and 2, but this is not the case, for the sign of 2 changes accordingly as it is compared with 3 or 1, as is apparent from the study of the model.

That is, the above expression for the configuration of grape-sugar permits of two interpretations, and to avoid confusion the structure is represented graphically as follows: By means of the flexible rubber models the molecules of the d. and l. saccharic acids are constructed; these are then placed upon a plane surface in such way that the carbon atoms lie in a straight line, when the hydrogens and hydroxyls arrange themselves on either side, and by projection present the following arrangements:

I.



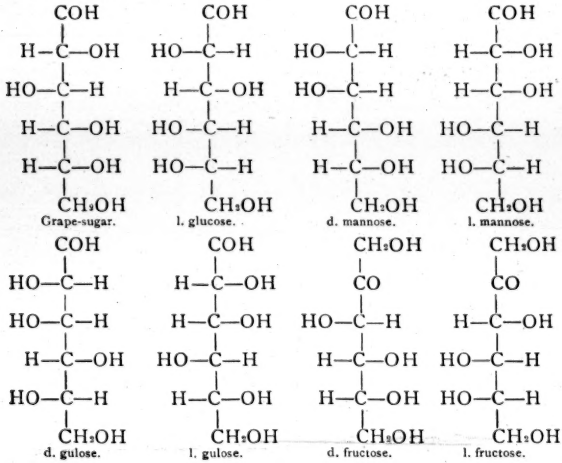
II.



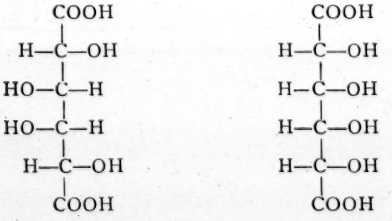
The same appearance is also obtained by the use of the inflexible wire models, arranging the carbon atoms in a vertical plane and regarding the structure from above. Fischer selects the first from

the two above expressions for the d. saccharic acid, whereby it is again immaterial if, at starting, the arrangement of hydrogen and hydroxyl upon the starred carbon atom does or does not follow the motion of the hands of a watch. From this, therefore, are derived the following graphic representations of the configurations of the d. glucose and its isomers, the same being projections of models constructed on the basis of the configurations already indicated by the + or — signs.

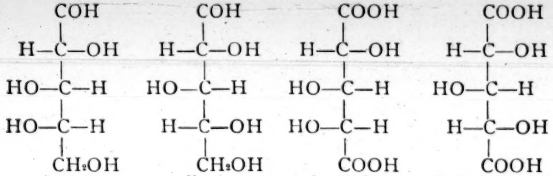
Of course these projection formulas have a quite different significance from others of similar *appearance* which have been proposed before.



The projections for the two inactive dibasic acids of the dulcit series, which probably exist as the mucic and allomucic acids, are also given, as possibly furnishing some insight into the configuration of the galactose.

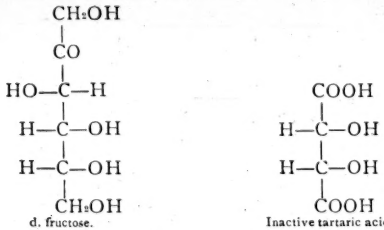


In the same way the following projections for the pentoses and their corresponding trioxy-glutaric acids are obtained:



Arabinose. Xylose. Active acid from Arabinose. Inactive acid from Xylose.

Working from these formulas, the models of the molecules are easily constructed in which the + or — arrangement of each asymmetric carbon atom is readily seen. Their value is also apparent in the study of such reactions as increase or decrease the number of asymmetric carbon atoms, as an example of which the oxidation of fruit-sugar or levulose to inactive tartaric acid is given. The comparison of the projection formulas of the two bodies renders it apparent how this reaction is possible.



d. fructose. Inactive tartaric acid.

Undoubtedly this insight thus obtained into the constitution and configuration of the sugars will point out the way to new reactions and to new explanations of known reactions; and in any event, Fischer's work, of which these last papers present the climax, constitutes the most notable contribution yet made to the subject.

PURDUE UNIVERSITY, *April*, 1892. W. E. STONE.

CONSTITUTION OF BENZENE.

In the last communication by von Baeyer[1] on the above subject the following passage occurs:

"The task which I set myself at the beginning of these investigations was to determine the constitution of benzene by experi-

[1] Annalen der Chemie **269**, 145.

mental methods, and not to prove the correctness of any hypothesis by experiment. Accordingly, I have changed my view repeatedly, as the sum of my experiences has seemed to speak more for one view or the other. If now I put prominently forward an hypothesis which I formerly opposed, I beg the reader not to be surprised, and not to accuse me of inconsistency, if later I should prefer another hypothesis."

"The hypothesis I refer to is that of Claus. It consists in the assumption that each carbon atom of benzene is united to the two adjoining atoms by ordinary single union, and to the carbon atom in the para position by a peculiar bond. I objected to this hypothesis mainly because such para-bonds could not be found in the reduction-products of the benzene-carbonic acids, and I therefore put forward the centric formula, which is intended to express the idea that the diagonal valencies of Claus are not united with each other, but are free and directed towards the center. I observed, however, that this formula is identical with that of Claus if in the case of the latter it be assumed that the rupture of a single para-bond caused both the others to go over into double bonds."

"I shall now, on the basis of new facts, attempt to prove that the formula of Claus agrees best with the facts, with this limitation, that para-bonds exist only as long as the benzene-nucleus remains intact." The author then shows that:

1. No conclusion as to the constitution of benzene can be drawn from the course of the reduction of a benzene-derivative; and

2. The reformation of a benzene-nucleus from a hydro-derivative can throw light upon the constitution of benzene.

And says: "The question as to the constitution of benzene is, however, not yet fully answered, because Claus' formula gives a definite picture of the structure of the benzene-molecule, only in case we assume that the carbon atoms of the molecule lie in a plane, and that the four valencies of each of these atoms correspond even in this condition to the four angles of a regular tetrahedron. . . . The material now available is, however, still too meager to lead to a definite conception of the space configuration of the benzene molecule. I consider, therefore, the solution of this stereochemical problem as the task that should next be undertaken, and I have begun the investigation of the reduction-products of isophthalic acid as well as of the carbonic acids of complex benzene-compounds." I. R.